Book of Abstracts
of the

# 12th International Conference
# on Electroanalysis

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Prague, Czech Republic
16–19 June 2008

European Society for ElectroAnalytical Chemistry

**Dear Colleagues, Friends,**

Welcome to **ESEAC 2008, the 12th International Conference on Electroanalysis**. This biannual meeting, which started in 1986 in Dublin and then passed through ten other European cities, has become a very important event, bringing together electroanalysts, both scientists with their students and practitioners, from all of the world. They present their results, exchange ideas, strengthen their friendships, create new relationships, deepen their cooperation and plan new projects. This year, **ESEAC** comes to Prague, one of the most beautiful and friendly cities of the world, which has a great tradition in scientific research and university teaching in general and in electrochemistry with electroanalysis in particular.

The Scientific and Organizing Committees have designed the **12th ESEAC** along the lines which have been tested and found reasonable during the previous meetings. There are several plenary and keynote lectures, summarizing and critically evaluating some important fields of contemporary electroanalysis, followed by more specialized oral and poster presentations. It is expected that a great role will be played by formal and informal discussions (do not forget, Prague is a historic city full of inspiring pubs, winehouses and coffeehouses; moreover, the beautiful natural setting of the Krystal Hotel, the neighbouring Divoká Šárka, invites for discussions during morning and/or evening jogging and walking).

To establish a general framework for the conference programme, the Scientific Committee has selected five principal topics to be treated, which definitely belong to the most progressive trends in the present-day electroanalysis. They involve *"New Electrode Materials"*, *"Modification of Electrodes with Biochemical and Nanostructured Systems"*, *"Electroanalytical Sensors and Detectors for Continuous and Flow-through Measurements"*, *"Environmental Electroanalysis"* and *"Hyphenation of Electrochemical and Other Measurements"*. Of course, their boundaries are diffuse and thus a number of conference contributions will penetrate through them; this is good, because the greatest development occurs at the borders.

The **12th ESEAC** has been organized by the Czech Chemical Society, in cooperation with the Faculty of Science, Charles University in Prague, and has been supported by many other subjects. Many thanks to all of them.

Have a nice time in Prague.

*Karel Štulík,*
*chairman of the Scientific Committee and*
*Jiří Barek,*
*chairman of the Organizing Committee*

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# General Information

### Organization

The conference is organized under the auspices of the European Society for ElectroAnalytical Chemistry.

### Conference Site

Hotel Krystal Prague, J. Martího 2/407, 162 00 Prague 6 - Veleslavín, Czech republic
Reception desk phone +420 220 563 411
Reception desk fax +420 220 561 627
Reservation desk phone +420 220 560 233
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e-mail krystal@cdms-krystal.cz

### Conference Office

The registration and secretary desk is located in the entrance hall of Hotel Krystal.
It will be open according to the following schedule:

| | |
|---|---|
| Sunday, June 15, 2008 | from 16.00 to 19:00 |
| Monday, June 16, 2008 | from 8:00 to 19:00 |
| Tuesday, June 17, 2008 | from 8:00 to 19:00 |
| Wednesday, June 18, 2008 | from 8:00 to 14:00 |
| Thurseday, June 19, 2008 | from 8:00 to 12:00 |

### Official Language

The official language of the conference is English. No simultaneous translation will be provided.

### Proceedings

Abstracts of all oral and poster presentations will be distributed to the participants at the beginning of the conference. Full text of some presentations will be published in a special issue of the journal Electroanalysis. Authors are requested to submit their manuscripts, observing following the format of the Journal, before July 15, 2008, using the Wiley electronic submission system and mentioning ESEAC 2008 in their cover letter.

### Oral Presentations

Oral presentations are 20 min long including discussion and speakers are asked to dowland their Power Point presentation on the local computer the before their talk.

### Poster Presentations

One display board will be provided for each poster. Poster board dimensions are 96 cm with and 130 cm height. The authors must use board with the label indicating their poster number. The posters starting with numbers PP001 should be put up on Monday, June 16, 2008 till 18:00 and removed at 21:00. The posters starting with numbers PP096 should be put up on Tuesday, June 17, 2008 till 18:00 and removed at 21:00.

### Social Programme

There will be an informal welcome on Sunday, June 15, 2008 from 17:00–20:00 at the conference site, allowing participants to register and to have a drink and snack and meet other participants. The social program also includes sightseeing of Prague on Wednesday afternoon and cocktail on Wednesday evening.

# Acknowledgements

The organizing and scientific committees wish to express their thanks to the sponsors an exhibitors whose help has made this conference possible:

- Bernard Brewery
- BASi (Bioanalytical Systems, Inc.)
- Budweiser Brewery
- BVT Technologies
- Czech Airlines
- Czech Chemical Society
- DropSens
- Electroanalysis
- Faculty of Science of Charles University in Prague
- International Society of Electrochemistry
- IJ Cambria Scientific
- Krušovice Brewery
- Megabooks CZ

# Program of oral presentations

| | Sunday 15 June | Monday 16 June | | Tuesday 17 June | |
|---|---|---|---|---|---|
| 8.20-8.40 | | **Openning ceremony** | | | |
| 8.40-9.00 | | | | **ESEAC 2010** | |
| 9.00-9.20 | | PL1 | | PL2 | |
| 9.20-9.40 | | **Trojanowicz** | | **Janata** | |
| 9.40-10.00 | | | | | |
| 10.00-10.20 | | KN1 | | KN2 | |
| 10.20-10.40 | | **Dunsch** | | **Walcarius** | |
| 10.40-11.00 | | Coffe | | Coffe | |
| | | Auditorium 1 | Auditorium 2 | Auditorium 1 | Auditorium 2 |
| 11.00-11.20 | | Polsky | Fraihat | Palecek | Skrzypek |
| 11.20-11.40 | | Dong | Redha | Lisdat | Songa |
| 11.40-12.00 | | Ivaska | Navrátil | Heyrovský | Tomčík |
| 12.00-12.20 | | Hocevar | Mousty | Ozsoz | Zaouak |
| 12.20-12.40 | | | | | |
| 12.40-13.00 | | Lunch | | Lunch | |
| 13.00-13.20 | | | | | |
| 13.20-13.40 | | 12:30-13:30 | | 12:30-13:30 | |
| 13.40-14.00 | | | | | |
| | | Auditorium 1 | Auditorium 2 | Auditorium 1 | Auditorium 2 |
| 14.00-14.20 | | Nyholm | Owino | Karyakin | Laschi |
| 14.20-14.40 | | Gorton | Ballarin | Kulesza | Crilly |
| 14.40-15.00 | | L'Her | Rudnitskaya | Keighley | Evans |
| 15.00-15.20 | | Flechsig | Jamal | Stojek | Litescu |
| 15.20-15.40 | | Daniele | Pauliukaite | Kalcher | Ithurbide |
| 15.40-16.00 | | Kazimierska | Shumyantseva | Ugo | Barek |
| 16.00-16.20 | **Registration** | Coffee | Coffee | Coffee | Coffee |
| 16.20-16.40 | | Leech | Lukaszewski | Beinrohr | Lesven |
| 16.40-17.00 | | Zuman | Zima | Mandler | Rassaei |
| 17.00-17.20 | **Welcome party** | Brett | Pedrero | Brainina | Rocha |
| 17.20-17.40 | | Fojta | de-los-Santos-Alvarez | Björefors | Ferrigno |
| 17.40-18.00 | | Stoica | Miranda-Castro | Ackermann | Nesměrák |
| 18.00-18.20 | | | | | |
| 18.20-18.40 | | Supper | | Supper | |
| 18.40-19.00 | | | | | |
| 19.00-19.20 | | 18:00-19:00 | | 18:00-19:00 | |
| 19.20-19.40 | | Poster session 1 | | Poster session 2 | |
| 19.40-20.00 | | with beer | | with beer | |
| 20.00-20.20 | | and snacks | | and snacks | |
| 20.20-20.40 | | sponsored by | | sponsored by | |
| 20.40-21.00 | | **ELECTROANALYSIS** | | **CSCH** | |
| | | 19:30-21:00 | | 19:30-21:00 | |

|  | Tuesday 17 June |  | Wednesday 18 June |  | Thursday 19 June |  |
|---|---|---|---|---|---|---|
| 8.20-8.40 |  |  |  |  |  |  |
| 8.40-9.00 | **ESEAC 2010** |  | **Poster award** |  |  |  |
| 9.00-9.20 | PL2 |  | PL3 |  | PL4 |  |
| 9.20-9.40 | **Janata** |  | **Katz** |  | **Erkang Wang** |  |
| 9.40-10.00 |  |  |  |  |  |  |
| 10.00-10.20 | KN2 |  | KN3 |  | KN4 |  |
| 10.20-10.40 | **Walcarius** |  | **Matysik** |  | **Kuhn** |  |
| 10.40-11.00 | Coffe |  | Coffe |  | Coffe |  |
|  | Auditorium 1 | Auditorium 2 | Auditorium 1 | Auditorium 2 | Auditorium 1 | Auditorium 2 |
| 11.00-11.20 | Palecek | Skrzypek | Ludvík | Mashazi | Tasca | Pesavento |
| 11.20-11.40 | Lisdat | Songa | Mocak | Larabi-Gruet | Ogorevc | Boldrin Zanoni |
| 11.40-12.00 | Heyrovský | Tomčík | Zhang | Ziyatdinova | Munoz |  |
| 12.00-12.20 | Ozsoz | Zaouak | Zuman | Lesniewski | Tharamani |  |
| 12.20-12.40 |  |  |  |  |  |  |
| 12.40-13.00 | Lunch |  | Lunch |  | Lunch |  |
| 13.00-13.20 |  |  |  |  |  |  |
| 13.20-13.40 | 12:30-13:30 |  | 12:30-13:30 |  | 12:30-13:30 |  |
| 13.40-14.00 |  |  |  |  |  |  |
|  | Auditorium 1 | Auditorium 2 |  |  | Auditorium 1 | Auditorium 2 |
| 14.00-14.20 | Karyakin | Laschi | Sightseeing of | Excursion | Zamuner |  |
| 14.20-14.40 | Kulesza | Crilly | Prague | to | Esplandiu |  |
| 14.40-15.00 | Keighley | Evans |  | Heyrovsky | Bilewicz |  |
| 15.00-15.20 | Stojek | Litescu |  | institute | **Closing Ceremony** |  |
| 15.20-15.40 | Kalcher | Ithurbide |  |  |  |  |
| 15.40-16.00 | Ugo | Barek |  |  |  |  |
| 16.00-16.20 | Coffee | Coffee |  |  |  |  |
| 16.20-16.40 | Beinrohr | Lesven |  |  |  |  |
| 16.40-17.00 | Mandler | Rassaei |  |  |  |  |
| 17.00-17.20 | Brainina | Rocha |  |  |  |  |
| 17.20-17.40 | Björefors | Ferrigno |  |  |  |  |
| 17.40-18.00 | Ackermann | Nesměrák |  |  |  |  |
| 18.00-18.20 |  |  |  |  |  |  |
| 18.20-18.40 | Supper |  |  |  |  |  |
| 18.40-19.00 |  |  |  |  |  |  |
| 19.00-19.20 | 18:00-19:00 |  |  |  |  |  |
| 19.20-19.40 | Poster session 2 |  | Coctail |  |  |  |
| 19.40-20.00 | with beer |  |  |  |  |  |
| 20.00-20.20 | and snacks |  | 19:30-22:00 |  |  |  |
| 20.20-20.40 | sponsored by |  |  |  |  |  |
| 20.40-21.00 | **CSCH** |  |  |  |  |  |
|  | 19:30-21:00 |  |  |  |  |  |

# PLENARY LECTURES

## PL1
## ENANTIOSELECTIVE ELECTROCHEMICAL SENSORS AND BIOSENSORS

**MAREK TROJANOWICZ**

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The chiral separation and selective determination of particular optical isomer of a given compound is a challenging task for contemporary chemical analysis. It is a problem of great importance for many areas of scientific research, as well as for various routine analytical applications. Most of biochemical systems functioning in living organisms involve chiral interactions resulting from different stereochemistry of numerous biologically active compounds. Reactions involving enzymes, functioning of transmitters and receptors, numerous metabolic pathways are most often stereoselective. Enantiomeric purity of various compounds is important in stereospecific synthesis, production of pharmaceuticals, pesticides and some food additives, where only one enantiomer may interact satisfactorily.

Chiral analysis is at present predominated by high performance chromatographic and electromigration methods that require advanced instrumentation and complex optimization of analytical procedures. Separations are based on the use of chiral stationary phases or chiral selectors, and their interactions with separated species may involve multiple hydrogen bonds, $\pi$–$\pi$ interactions, dipole-dipole and ionic interactions. The same interactions might be employed in design of chemical or biochemical enantioselective sensors, hence determination of particular enantiomer with the use of enantioselective sensor or biosensor might be a potential alternative for numerous routine analytical applications might. Successful design of such sensors, however, is a great challenge compared e.g. to chromatographic methods, where separation of optical isomers is a result of multiple unit operations of separation in each measurement.

The search for such electrochemical sensors can be dated back to late 1970-ties, when enantioselectivity of some potentiometric ion-selective electrodes with neutral carriers in the plasticized membranes was observed. Generally, however, it did not attract desired attention in development of electrochemical sensors. Compounds employed as chiral selectors in separation methods involve cyclodextrins, natural polysaccharides and their derivatives, macrocyclic antibiotics, chiral crown ethers, calixarenes, proteins, chiral surfactants, and ligand-exchange complexes. They can be employed also as potential ionophores in electro-chemical sensors. As chemically active species providing enantioselectivity of sensors can be also used ion-channels in ion-selective electrodes, enzymes for determination of substrates or inhibitors in amperometric biosensors, doped conducting polymers in potentiometric or piezoelectric sensors, enantioselective antibodies in piezoelectric and micro-electromechanical devices, or molecular imprinted polymers in potentiometric sensing. The possibility of the use of kinetic effects in chiral recognition is still an interesting field for investigation with potential application e.g. in fast flow-injection measurements based on recording of transient signals.

## PL2
## INTEGRATED CHEMICAL ELECTRONICS IN ANALYSIS

**JIRI JANATA**

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Integration of chemical recognition elements with solid state electronic devices has been subject of intense interest for over three decades, with some notable achievements achieved in electroanalytical chemistry. Initially, the “chemistry” has been added to more or less conventional silicon electronics with ensuing advantages in miniaturization, noise reduction and promise of multivariate analysis. That was the era of chemically sensitive field-effect transistors (CHEMFET), i.e. ion-sensitive field-effect transistors and enzymatic field-effect transistors. In the second phase, it has been recognized that modulation of electronic properties of organic semiconductors leads to creation of solid state work function sensors for gases, again based on the traditional silicon platform.

Development of organic electronics took place almost in parallel. In that case silicon, as the functional material, has been replaced with organic semiconductors. The motivation for this development has been the promise of flexible and inexpensive electronics. What has not been recognized is that the physics of operation of so-called organic field-effect transistors (OFET) is fundamentally different from the physics of their silicon-based counterparts. In the last decade the chemically responsive OFETs have been added to the toolbox of electroanalytical chemistry.

All chemically sensitive silicon based field-effect transistors are high input impedance potentiometric sensors. In such case the transistor current passes only through silicon, which is protected from the environment by nearly ideal passivation by silicon dioxide/silicon nitride. The corollary of this fact is that WF of silicon does not change and the WF-FET sensors do not require separate reference electrode. On the other hand in OFETs the transistor current passes through the organic semiconductor, which is subject to modulation by the operating environment. The chemical response to gases and vapors then has its origin in multiple points in the device. The contacts, the bulk of the organic semiconductor and all interfaces can be involved making the interpretation of the response exceedingly difficult. Because of this OFETs are chemiresistors and belong to the class of conductimetric chemical sensors.

REFERENCES

1. Janata J., Josowicz M.: Nature Materials *2* (1), 19 (2003).
2. Hang Chen, Rambathla A., Potje-Kamloth K., Janata J.: J. Electrochem. Soc. *154*, H453 (2007).

## PL3
## BIOCOMPUTING SYSTEMS BASED ON ELECTRICALLY WIRED ENZYMES

EVGENY KATZ* and MARCOS PITA

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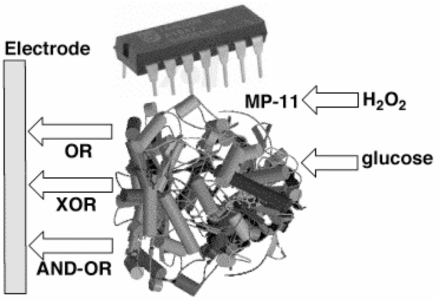
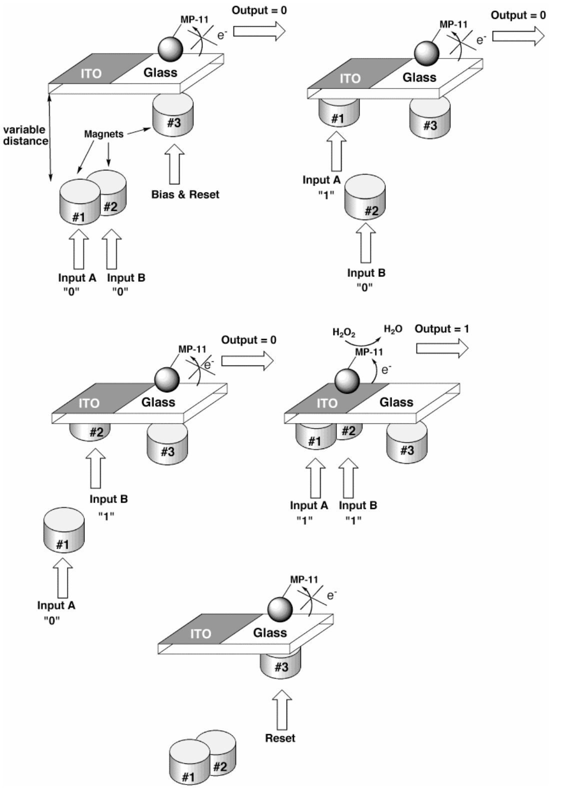
Biochemical computing is an exciting new field, which shows great promise, but at the same time faces substantial challenges. Recently designed logic gates based on enzyme-catalyzed reactions allowed logic operations and simple computing in solutions with the optical read-out of the output signals.

The present paper reports on the logic gates based on electrically wired enzymes associated with electrode surfaces[1]. Logic gates performing Boolean operations were developed using bioelectrocatalyzed reactions of redox-enzymes and their assemblies with electron transfer mediators and cofactors. The electrochemical read-out of the output signals from the immobilized enzyme-assemblies was achieved, thus converting the biochemical logic gates into real bioelectronic systems. The reconfigurable logic gate produced different logic operations “OR”, “XOR”, “AND-OR” depending on the potential applied on the enzyme-functionalized electrode, Scheme 1. Future application of multi-electrode arrays functionalized with various enzyme-based logic gates is envisaged. This will finally result in bioelectronic computing chips that will interface biological and electronic systems.

In another approach biocatalyst-modified magnetic nanoparticles were applied to generate electrochemically readable logic output signals upon applying variable magnetic input signals[2]. The logic gate operation was based on the translocation of the magnetic nanoparticles between conducting and non-conducting domains of the solid support, Scheme 2.



Scheme 1. **The electrode functionalized with glucose oxidase (GOx) and microperoxidase-11 (MP-11) performs various Boolean logic operations (OR, XOR, AND-OR) upon addition of glucose and/or $H_2O_2$ and application of different potentials**



Scheme 2. **Magneto-activated logic operation “AND” performed by the biomolecular-functionalized magnetic nanoparticles**

The enzyme-based system can be adapted to various chemical signals and their combinations to perform logic operations of different kind and complexity by integrating different enzymes with the electrochemical interface. Integration of several enzymes with the electrode support will allow scaling up the biocomputing network where the connections between the enzymes will be maintained through the exchange of substrates/products of the biochemical reactions, and the final output signal will be transduced into the electrical current.

*This research was supported by NSF grants DMR-0706209 and CCF-0726698.*

REFERENCES

1. Pita M., Katz E.: J. Am. Chem. Soc. 130, 36 (2008).
2. Vasilyev S., Pita M., Katz E., Electroanalysis 20, 22 (2008).

## PL4

## RECENT PROGRESS FOR SIMPLE APPROACH ON NANOMATERIAL ASSEMBLIES AND FUNCTIONAL SUPERSTRUCTURES

**ERKANG WANG**

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Nanostructured materials represent one of the most dynamic areas of modern science. The interest of these systems is due to the remarkble and unusual properties when at least one dimension in the nanometer scale. Methods of fabrication for one-, two- and three dimensional nanostructures differ vastly, among which template-directed methods are usually used.

Here, we report some recent progress from our laboratory on the preparation of noble metal nanoparticles, disks, sheets, spheres, and also conducting polymer nanobelts by simple wet chemical routes without templates.

A heat-treatment based strategies for one-step synthesis of size-controlled gold and silver nanoparticles were carried out successfully. Large-scale and rapid synthesis of uniform poly (*o*-phenylenediamine) nanobelts was performed without templates and surfactants. Large-scale preparation for 2D structure of single crystallines including nanoplates and microdisks of gold was realized. Submicrometer-scale, monodisperse, spherical colloid of coordination polymers were formed in solutions. Some microstructures, as metal nanoparticles/polymer, were made through layer-by-layer assembly on solid substrate and in solution either, showing unique functionalities. Diameter-controlled 3D flowerlike superstructure of gold could be rapidly obtained by eletrochemical methods. Different superstructures composed of nanoparticles and polymer film for solid state electrochemiluminescence using Ru $(bpy)_3^{2+}$ were prepared, exhibiting excellent ECL signal with high stability. Interestingly, a general route to transfer normal hydrophilic cloths into superhydrophobic surfaces are proposed with potential applications.

*The finacial support from National Natural Science Foundation of China is greatly appreciated.*

# KEYNOTES

## KN1
## CONJUGATED POLYMERS AND OLIGOMERS AS ELECTRODE MATERIALS

**LOTHAR DUNSCH**

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The lecture presents an overview on the application of conducting polymers and oligomers as electrode materials. The special state of this type of an organic material as a semiconductor with charged states like polarons, bipolarons and polaron pairs created by electrochemical doping is discussed. It is shown that the electronic state of a conducting polymer can be studied in detail by *in situ* ESR/UV/Vis/NIR spectroelectrochemistry at electrodes in dependence on the potential[1,2]. While the bulk of metal electrodes is not available for an uptake of organic structure this can be managed in conducting polymer electrodes and applied for the analysis of special paramagnetic molecules[3]. Furthermore it is possible to prepare micro-structured polymer electrodes for electrochemical and spectroelectrochemical applications[4]. Conducting polymers like polyaniline, polypyrrole or polythiophene are applied in electrochemical structure both for the contact at the electrode as well as for a membrane for sensing. In the latter case a functionality is introduced in the polymer backbone or as a side group[5]. This can be done by electrochemical copolymerisation or chemical reactions at a preformed polymer backbone. It is shown that the copolymerisation of different 3-substituted monomers changes the charged state of the copolymer which can be used in electroanalysis. Another type of functionalised polymers for analytical applications are backbone functionalised polymers like polysalenes[6]. The state of the conducting polymer is characterised by interactions of the paramagnetic metal ions with spin states at the organic ligands in the polymer. The electroanalytical use of such a special interaction in a polymer chain is described in detail here[6].

An outlook is given on future developments of the use of conduction polymers as electrode materials.

REFERENCES

1. Dunsch L., Petr A.: Ber. Bunsenges. Phys. Chem. *97*, 436 (1993). Petr A., Dunsch L., Neudeck A:: J. Electroanal. Chem. *153*, 412 (1996).
2. Rapta P., Dunsch L.: J. Electroanal. Chem. *22*, 506 (2001); Neudeck A., Petr A., Dunsch L.: J. Phys. Chem., B *912*, 103 ( 1999).
3. Rapta P., Bartl A., Dunsch L.: Polymer Bull. *37*, 751 (1996); Rapta P., Bartl A., Dunsch L.: Synth. Met. *84*, 187 (1997).
4. Rapta P., Neudeck A., Bartl A., Dunsch L.: Electrochim. Acta *44*, 3483 (1999).
5. Aubert P.-H., Neudeck A., Dunsch L., Audebert P., Capdevielle P., Maumy M.: J. Electroanal. Chem. *77*, 470 (1999); Tarábek J., Jähne E., Rapta P., Ferse D., Adler H.-J., Dunsch L.: Elektrokhimiya *42*, 1169 (2006).
6. Tarábek J., Rapta P., Jähne E., Ferse D., Adler H.-J., Maumy M., Dunsch L.: Electrochim. Acta *50*, 1643 (2005); Tarábek J., Rapta P., Kalbáč M., Dunsch L.: Anal. Chem. *76*, 5918 (2004).

## KN2
## FUNCTIONALIZED AND MESOSTRUCTURED SILICA FILMS ON ELECTRODES

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The aim of this lecture is to highlight and discuss some recent achievements performed with sol-gel-derived silica and organosilica films in electroanalytical chemistry[1,2]. Three complementary directions will be considered. The first one relies on the usefulness of electrochemical techniques to get information on mass transport through ordered mesoporous films, with special emphasis on the influence of the mesostructure type and the nature of the redox probe on these processes[3]. The second aspect concerns a feedback of materials science to electroanalysis, by exploiting the attractive and sometimes unique properties of mesoporous (organo)silica films on electrodes to improve their sensitivity in comparison to the non-ordered ones, when applied as voltammetric sensing devices[4,5]. The third domain is related to the use of electrochemistry to prepare thin films of sol-gel-derived (organo) silica films, via a rather novel electrochemically-driven deposition method[6]. This involves basically the formation of a self-assembled monolayer of mercaptopropyl-trimethoxysilane on a gold electrode, which is then transferred to a silica sol containing the hydrolyzed precursors where a cathodic potential is applied to increase pH locally at the electrode/solution interface and to induce co-condensation of the precursors[7]. Special attention will be given to highlight the effect of the electrodeposition conditions (applied potential and duration) on the film formation mechanism and on its properties[8]. The possibility and the interest to prepare ordered and oriented mesoporous films by this method will be also discussed[9].

REFERENCES

1. Walcarius A., Mandler D., Cox J., Collinson M. M., Lev O.: J. Mater. Chem. *15*, 3663 (2005).
2. Walcarius A.: C. R. Chim. *8*, 693 (2005).
3. Etienne M., Quach A., Grosso D., Nicole L., Sanchez C., Walcarius A.: Chem. Mater. *19*, 844 (2007).
4. Etienne M., Walcarius A.: Electrochem. Commun. *7*, 1449 (2005).

5. Etienne M., Walcarius A.: Electroanalysis *19*, 129 (2007).
6. Sayen S., Walcarius A.: Electrochem. Commun. *5*, 341 (2003).
7. Walcarius A., Sibottier E.: Electroanalysis *17*, 1716 (2005).
8. Sibottier E., Sayen S., Gaboriaud F., Walcarius A.: Langmuir *22*, 8366 (2006).
9. Walcarius A., Sibottier E., Etienne M., Ghanbaja J.: Nature Mater. *6*, 602 (2007).

## KN3
## HYPHENATION OF ELECTROCHEMICAL AND OTHER METHODS

**FRANK-MICHAEL MATYSIK**

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Instrumental analytical methods have experienced a rapid development during recent years. Miniaturization, the increasing impact of mass spectrometry (MS) and the implementation of hyphenated systems have become trend-setting routes towards enhanced performance characteristics. In particular, the design of tailor-made electrochemical systems with a wide variety regarding size, geometry and materials is an essential strength that can be exploited for the construction of hyphenated analytical arrangements. The present contribution presents several examples that illustrate the possibilities of implementation of electrochemical components into more or less complex hyphenated systems.

Electrochemical detection (ED) in conjunction with high performance liquid chromatography (HPLC) is a traditional field of electroanalysis and has been applied to a wide range of analytical problems[1]. One limitation of ED in conjunction with HPLC is that the ED baseline response is rather sensitive to changes in the composition of the eluting solution which presents a problem in gradient-elution protocols. A new approach of liquid chromatographic separations is the so-called stationary phase optimized liquid chromatography[2] (POPLC) concept where segmented columns of different stationary phases are combined in an optimized way such as to achieve tailor-made selectivity under isocratic conditions. This approach offers new chances for the implementation of ED with excellent performance characteristics. Examples will be discussed in the field of determinations of explosives using POPLC-UV-ED[3].

Another option of implementation of electrochemical methods into flow-stream analysis systems is the so-called electrochemically assisted injection[4] (EAI) where the analyte is converted electrochemically during the injection step. This concept will be discussed in conjunction with capillary electrophoresis (CE).

Finally, the enormous potential of time-of-flight mass spectrometry (TOF-MS) hyphenated to CE will be illustrated. A hyphenated system consisting of EAI-CE-TOF-MS will be introduced and preliminary results will be presented.

*Financial support by the Deutsche Forschungsgemeinschaft (MA 1491/7-1) is gratefully acknowledged.*

REFERENCES

1. Stulík K., Pacáková V.: *Electroanalytical Measurements in Flowing Liquids*, Ellis Horwood, Chichester 1987.
2. Nyiredy Sz., Szücs Z., Szepesy L.: J. Chromatogr., A *1157*, 122 (2007).
3. Matysik F.-M., Schumann U., Engewald W.: Electroanalysis *20*, 98 (2008).
4. Matysik F.-M.: Electrochem. Comm. *5*, 1021 (2003).

## KN4
## RATIONAL DESIGN OF ELECTRODES FOR BIO-ANALYSIS

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Over the last decades the subject of complex interfaces has moved to the forefront of numerous original studies. The possibility to engineer precisely interfaces is playing an increasingly important role in the development of new technologies relevant to all aspects of our live ranging from energy conversion to biomedical devices. Engineering of surfaces and interfaces simultaneously at different length scales, from the molecular to the macroscopic size, using self-ordering phenomena and growth processes can be steered to create a wide range of structures that allow the understanding of how structural features control the function of such systems. Here we present electrodes developed in the last few years using approaches that allow us to tailor their physico-chemical properties at several length scales. We'll especially focus on organized porous electrode systems[1–3], carbon nanotube fiber microelectrodes[4,5] and individually modified carbon nanotubes as ultimate electrodes[6] for bioelectroanalysis.

REFERENCES

1. Szamocki R., Reculusa S., Ravaine S., Bartlett P. N., Kuhn A., Hempelmann R.: Angew. Chem. Int. Ed. *45*, 1317 (2006).
2. Szamocki R., Velichko A., Holzapfel C., Mucklich F., Ravaine S., Garrigue P., Sojic N., Hempelmann R., Kuhn A.: Anal. Chem. *79*, 533 (2007).
3. Szamocki R., Velichko A., Mucklich F., Reculusa S., Ravaine S., Neugebauer S., Schuhmann W., Hempelmann R., Kuhn A.: Electrochem. Comm. *9*, 2121 (2007).
4. Viry L., Derre A., Garrigue P., Sojic N., Poulin P., Kuhn A. : J. Nanoscience & Nanotechnology *7*, 3373 (2007).
5. Viry L., Derre A., Garrigue P., Sojic N., Poulin P., Kuhn A. : Anal. Bioanal. Chem. *389*, 499 (2007).
6. Warakulwit C., Nguyen T., Majimel J., Delville M.-H., Lapeyre V., Garrigue P., Ravaine V., Limtrakul J., Kuhn A. : NanoLett *8*, 500 (2008).

# ORAL PRESENTATIONS

## OP01

## VISUALISATION OF THE CATALYTIC ACTIVTY OF ENZYME-REDOXPOLYMER SPOTS FOR OPTIMISATION OF A BIOFUEL CELL CATHODE USING REDOX COPMTETITION SCANNING ELECTROCHEMICAL MICROSCOPY (RC-SECM)

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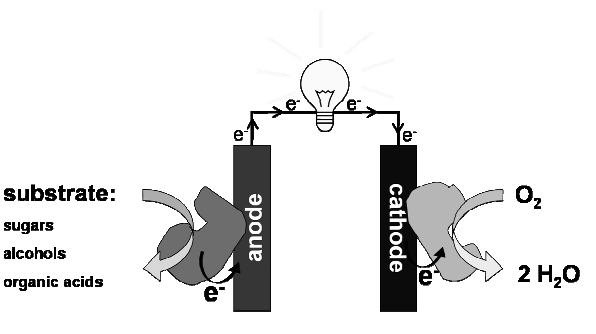
Biofuel cells are power generating devices which use environmental friendly fuels like sugars, alcohols, organic acids or oxygen at anode and cathode, respectively. The reactions at both electrodes are catalysed by biocatalysts such as enzymes or whole organisms. In addition, redox mediators are often used to increase the electron transfer rate between the active site of the biocatalyst and the electrode. If both, biocatalyst and mediator are securely fixed on the electrode surface no separator membrane in between anode and cathode compart-ment is needed (Scheme 1). Thus, integrating all necessary components on the electrode surface facilitates miniaturisation of biofuel cells.

Os-modified anodic electrodeposition paints can be used as redox polymers for wiring suitable enzymes to electrode sur-faces. Their redox potentials and the electron transfer charac-teristics can be fine tuned by different coordinating ligands at the active Os redox centre. Optimisation of this multi-para-meter system is rather complex, however, it is evident that improved electrode architectures are crucial for optimization of biofuel cells with respect to increased power output.

Redox-competition mode scanning electrochemical microscopy (RC-SECM)[1] is used for the optimisation of a biofuel cell cathode[2,3]. This SECM mode opens the opportunity for visualisation of catalyst activity with respect to the oxygen reduction reaction (ORR) with high lateral resolution. Spot arrays consisting of an enzyme-redox polymer mixture are produced using piezoceramic-based microdispenser. Utilisation of this automated spot-preparation system enables the forma-tion of reproducible spots of the same size and amount of deposited substances. RC-SECM is a fast and reliable method for monitoring and characterising of the ORR at a number of enzyme-redox polymer spots. Figure 1 shows a 3D picture of a laccase-redox polymer spot.



Scheme 1. **Schematic setup of a membrane-less enzyme based biofuel cell**

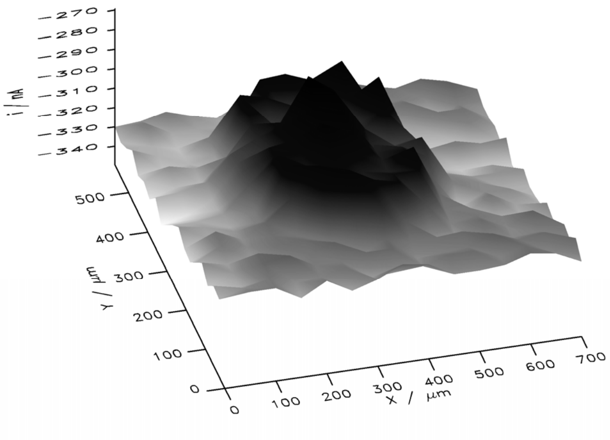


Fig. 1. **3D RC-SECM picture of a laccase-redox polymer spot**. Darker areas represent higher catalytic acti-vity at the sample

REFERENCES
1. Eckhard K., Chen X., Turcu F., Schuhmann W.: PCCP *8*, 5359 (2006).
2. Karnicka K., Eckhard K., Guschin D., Stoica L., Kulesza P., Schuhmann W.: Electrochem. Commun. *9*, 1998 (2007).
3. Ackermann Y., Guschin D., Maljuschka A., Eckhard K., Schuhmann W., Shleev S.: submitted.

## OP02

## ELECTROCATALYTIC ACTIVITY OF ITO ELECTRODES MODIFIED WITH METAL NANOPARTICLES

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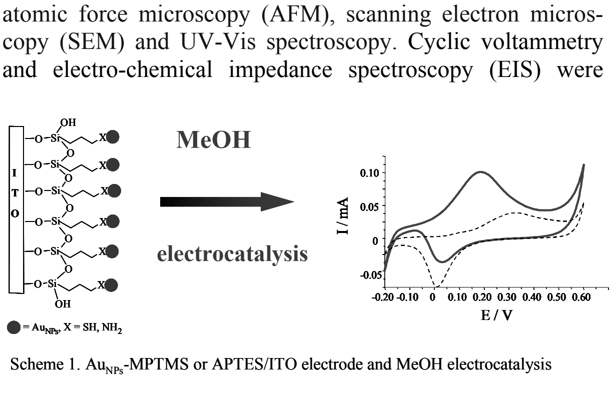
In recent years, the surface modification of electrodes with metal nanoparticles (NPs) has led to some of the latest developments in the field of electrochemical sensors. To date gold nanoparticles (AuNPs) are the most extensively studied because of their unique size-dependent physical, optical and electronic properties when compared to bulk gold[1]. Moreover, also platinum nanoparticles (PtNPs) have evoked increasing interest in the design of sensors and some reports have demonstrated that platinum nanoparticles can facilitate the electron transfer and increase the surface areas with enhanced mass transport characteristics[2].

All the properties displayed by metal nanoparticles are dependent on a combination of factors including preparative route, size, support and assembling methods, therefore it is not surprising that several studies have been dedicated to analyze the role played by each factor[3]. Various methodologies have been used for tailoring nanosized particles on electrode surfaces as covalent linkage, electrochemical deposition, grafting on assembled molecules with proper functional groups, etc.[4,5]. Among them the self-assembling approach represents a simple, fast, and versatile method to obtain 2D or 3D nanoparticles arrays in which both coverage and spatial distribution can be easily controlled[6]. The bifunctional crosslinkers 3-mercaptopropyltrimethoxy silane (MPTMS) and 3-aminopropyltriethoxysilane (APTES), are among the most common organosilanes used for colloidal immobilization[7].

An alternative fast and easier method to obtain nanoparticles modified electrodes is electrosynthesis; in such a way, by controlling the value and the length of the potential application it is possible to control size and amount of the nanoparticles grown up[8]. Methanol oxidation and oxygen reduction catalysed by metal NPs, especially PtNPs, have received considerable attention in the last few years. Both reactions are of prime importance in many vital applications including the electrochemical energy conversion in fuel cell and metal air batteries, as well as corrosion and several other industrial processes[9].

Herein, we report a study of the effects of two binding agents, MPTMS and APTES, attached as monolayer on Indium Tin Oxide (ITO) electrodes, on the electrochemical and catalytic activity of Ag, Au and Pt nanoparticles. The electrocatalytic activity for methanol oxidation and oxygen reduction of the metal NPs supported on ITO glass was explored in alkaline media. Furthemore, the electrochemical and electrocatalytic activity are compared with those of the same metal nanoparticles directly electrodeposited on ITO glass (see Scheme 1).

The morphology of the NPs layers, which depends on the way and the time of grafting, was investigated by using atomic force microscopy (AFM), scanning electron microscopy (SEM) and UV-Vis spectroscopy. Cyclic voltammetry and electro-chemical impedance spectroscopy (EIS) were employed to compare the electrochemical behavior of the investigated nanosized arrays.



Scheme 1. $Au_{NPs}$-MPTMS or APTES/ITO electrode and MeOH electrocatalysis

REFERENCES
1. Daniel M. C., Astruc D.: Chem. Rev. *104*, 293 (2004).
2. Chang G., Oyama M., Hirao K.: J. Phys. Chem., B *110*, 1860 (2006).
3. Maye M. M., Luo J., Lin Y., Engelhard M. H., Hepel M., Zhong C.-J.: Langmuir *19*, 125 (2003).
4. Tseng J.-Y., Lin M.-H., Chau L.-K.: Colloids Surf., A *182*, 239 (2001) and literature therein.
5. Zhang J., Kambayashi M., Oyama M.: Electrochem. Commun. *6*, 683 (2004).
6. Freeman R. G., Grabar K. G., Allison K. J., Bright R. M., Pavis J. A., Guthrie A. P., Hommer M. B., Jackson M. A., Smith P. C., Walter D. G., Natan M. J.: Science *267*, 1629 (1995).
7. Daniel M. C., Arstuc D.: Chem. Rev. *104*, 293 (2004).
8. Scavetta E., Stipa S., Tonelli D.: Electrochem. Commun. *9*, 2838 (2007).
9. Narayanan S. R, Valdez T. I, in: *Handbook of Fuell Cell: Fundamentals Technology and Applications*, (Vielstich W., Gastinger H. A., Lamm A., ed.), Vol. 4. John Wiley, Chichester 2003.

## OP03

## NEW ELECTRODE MATERIALS FOR DETERMINATION OF GENOTOXIC SUBSTANCES

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There is an ever increasing demand for the determination of extremely low concentrations of various genotoxic substances in complex environmental or biological matrices. Modern voltammetric and amperometric techniques can be used for determination of electrochemically reducible or oxidisable genotoxic substances because of their high sensitivity, sufficient selectivity (especially in combination with a suitable preliminary separation) and low cost, which make them suitable for large-scale monitoring[1]. There is a constant search for new electrode materials suitable for this challenging task. We will report our recent result regarding the determination of submicromolar and nanomolar concentrations of electrochemically reducible genotoxic substances with various types of amalgam electrodes[2] (meniscus modified silver solid amalgam electrode, silver solid composite amalgam electrode, amalgam paste electrode based either on mixture of solid silver amalgam with a suitable organic pasting liquid or on silver amalgam paste containing lower amount of silver) and on boron doped diamond film electrode[3]. Moreover, we will report our results regarding voltammetric and amperometric determination of electrochemically oxidisable genotoxic substances (e.g. aromatic or heterocyclic hydroxy or amino compounds) both on boron doped diamond film electrodes and carbon paste electrodes based on glassy carbon micro beads, which are compatible with high content of organic solvent in measured solutions[4]. Attention will be paid to electrochemical pretreatment, renewal of the electrode surface and to other procedures minimizing problems with electrode passivation which prevent broader use of electroanalytical methods in practice.

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REFERENCES
1. Barek J., Fischer J., Navratil T., Peckova K., Yosypchuk B., Zima J.: Electroanalysis *19-20*, 2003 (2007).
2. Danhel A., Peckova K., Cizek K., Barek J., Zima J., Yosypchuk B., Navratil T.: Chem. Listy *101*, 144 (2007).
3. Cizek K., Barek J., Fischer J., Peckova K., Zima J.: Electroanalysis *19*, 1295 (2007).
4. Zima J., Dejmkova H., Barek J.: Electroanalysis *19*, 185 (2007).

## OP04

## LIQUID CRYSTALLINE CUBIC PHASES FOR HOSTING ENZYMES - FROM BIOELECTRODES TO BIOFUEL CELLS

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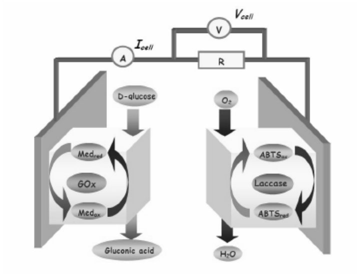
Lipid liquid-crystalline cubic phases are naturally fitted with a network of water channels by which substrate and product of catalytic reactions can be transported. Monoolein liquid-crystalline films are proposed as a convenient matrix to fix biocatalysts at the electrode surfaces. The material keeps the enzymes active and close to the electrode surface. It is non-toxic and biodegradable which is important in case of applications of the devices in the biological environment. At hydration over 20 % the cubic phase is stable in aqueous solutions. Doping MO with 1,2-dioleoyl-sn-glycero-3-phosphate increases the shear strength of the MO/$H_2O$ cubic phase and makes the aqueous channels walls anionic allowing for more stable immobilization of cationic mediators inside the cubic phase due to electrostatic interactions.

The role of biofuel cells is to convert the chemical energy into electrical current using redox enzymes as biocatalysts. The main advantage of this type of fuel cell is the application of natural compounds eg. glucose or ethanol, as fuels. Using the monoolein cubic phase for hosting the enzymes allowed to avoid any additional separating membranes in the biofuel cell. The membraneless biofuel cell (BFC) based on glucose oxidase and laccase as anodic and cathodic catalyst, respectively, was prepared. The mutant of filamentous fungi Aspergillus niger AM-11 from the culture collection of the Department of Industrial Microbiology (M. C. Sklodowska University, Lublin, Poland) was used as a source of glucose oxidase (GOx). Laccase from Cerrena unicolor C-139 was obtained from the culture collection of the Regensberg University and deposited in the fungal collection of the Department of Biochemistry (Maria Curie-Sklodowska University, Poland) under the strain number 139. Cabbage peroxidase was used to eliminate hydrogen peroxide in the compartment.



To increase the rate of the electron transfer from the enzyme to the electrode surface we applied a set of different mediators. Mediators were bound covalently or adsorbed on single walled carbon nanotubes (SWNTs) which lead to the increase of the electrode working area, eliminated leaching of the mediator to the solution and improved the conductivity of the system.

REFERENCES
1. Bilewicz R., Rowiński P., Rogalska E.: Bioelectrochemistry *66*, 3 (2005).
2. Nazaruk E., Bilewicz R.: Bioelectrochemistry *71*, 8 (2007).

## OP05

## ELECTROANALYSIS: NANOPARTICLES AS MODIFIERS AND MARKERS

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Nanomaterials have been used as:
- transducers for biosensors, immunosensors and chemical sensors;
- markers for immunosensors;

Magnetic nanoparticles were employed in immunoassay with magnetic separation.

1. It was shown, that behavior of the preliminary synthesized nanoparticles is analogous to the behavior of the metal in the 3rd energy state[1]. Moreover, application, for example, of Au or Bi nanoparticles modified screen printed graphite transducer is accompanied by appearing of good shaped stripping voltammograms of Hg (on Au) or Pb, Cd and Zn (on Bi) being deposited from more diluted solutions, than if macro or micro Au or Bi particles/layer coated electrodes are used. As a result, the detection limit decreases considerably.
2. Magnetic $Fe_3O_4$ nanoparticles, which were synthesized in reverse micelles, were used as markers in electrochemical immunoassay. An immunocomplex of the antibodies immobilized on the transducer surface and Salmonella typhimurium cells containing the nanomarkers was detected using stripping voltammetric analysis of the solution obtained after nanoparticles dissolving.
3. The interaction of nanomaterial (rates of adsorption, penetration and accumulation) with living cells was investigated with the use of spermatozoa and. $Fe_3O_4$ nanoparticles. The last one concentration was determined as in abovementioned case.

Thus, the information on: behavior of transducer containing nanoparticles, the use of magnetic nanomarkers and magnetic separation create the possibility to develop new sensors and approaches for the study into the interaction between nanomaterials and living cells.

*The authors are very grateful to ISTC (project 3230) and RFBR (projects 07-03-96070-p_ural_a and 07-03-96068-p_ural_a) for their financial support.*

REFERENCE

1. Brainina Kh., Neiman E.: *Electroanalytical Stripping Methods*. J. Wiley & Sons, NY 1993.

## OP06

## MEASUREMENT OF BISPHENOL A IN RIVER WATER USING SCREEN-PRINTED CARBON ELECTRODE USING CATIONIC SURFACTANT

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The effects and occurrence of organic species associated with disruption of the endocrine function have become increasingly important, since they can cause serious problems even when they are present at very low concentrations. Bisphenol A (4,4-(1-methylethylethylidene) bisphenol) is one of the potential endocrine disruptors, which may alter normal hormonal function. It is widely distributed in the natural environment, as well in surface water as important chemical used principally in the manufacture of several chemical products including epoxy resins and polycarbonate-derived products[1,2]. Although, bisphenol can be easily oxidized, the main problem associated with its electroanalytical determination on carbon electrodes is the fouling of electrode surface by the electropolymerized film, which suppresses the voltammetric signal hindering the construction of an analytical curve with enough accuracy[3]. The present work describes an eletroanalytical method based on square-wave voltammetry (SWV) using disposable screen-printed carbon electrodes (RRPE1001C Pine) in the presence of a cationic surfactant cetyltrimethylammonium bromide (CTAB) for determi-nation of BPA in river water. Electrochemical analyses were performed using an Autolab PGSTAT-30 (Eco Chemie). The disposable screen printed carbon electrodes (Pine Instruments) is based on a polymeric base 61 mm long, 15 mm wide and 0.36 mm of thick, where a working, reference and the auxiliary electrodes are exposed onto the surface. The working and auxiliary electrodes are made by carbon conducting ink and the reference electrode is Ag/AgCl. The measurements were performed in a conventional electrochemical cell of 10.0 mL, where the screen-printed carbon electrode was coupled. Solution of bisphenol was prepared in methanol. River water sample was collected from river Santa Maria do Leme, São Carlos, Brazil.

Bisphenol A (BPA) $1\times10^{-4}$ mol $L^{-1}$ is oxidized at 0.5 V on the screen-printed carbon electrode, which height intensity is duplicated in the presence of $7.5\times10^{-4}$ mol $L^{-1}$ of CTAB, as shown Fig.1. The effect was evaluated for different proportion of CTAB/BPA and the peak height increases up to [CTAB]/[bisfenol A] 2:1. The peak is dramatically decreased at higher concentration when the system reaches the critical micelar concentration. So, all the further studies were carried out for maximum proportion of [CTAB]/[bisfenol A] 2:1.

The square wave voltammetry technique was chosen to monitor the signal and the best conditions of analysis were: pH 8, frequency ($f$) of 60 Hz, scan increment ($\Delta E_s$) of 6 mV, pulse amplitude ($E_{sw}$) of 50 mV. The repeatability of the proposed sensor, evaluated in term of relative standard deviation presented values of 1% for 10 experiments in 0.11 ppm BPA using the same screen-printed electrode, indicating that the

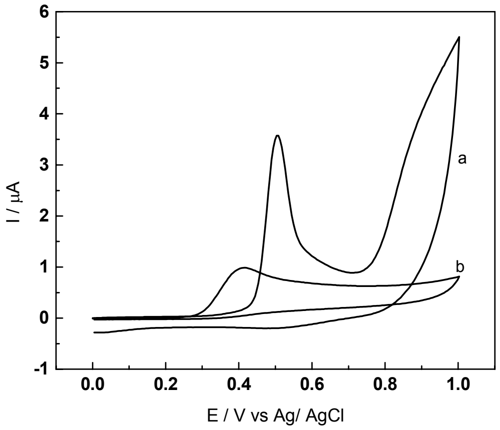

Fig. 1. **Cyclic voltammograms** obtained for $1\times10^{-4}$ mol $L^{-1}$ of BPA in Britton-Robison buffer (pH 7) on screen- printed carbon electrodes (a) without and (b) with $7.5\times10^{-4}$ mol $L^{-1}$ CTAB surfactant. Scan rate: 100 $mVs^{-1}$

surfactant presence avoid surface fouling and the electrode can be monitor at least 10 measured .

Using the optimal experimental conditions was constructed an analytical curve, which presents a linear relationship from 0.07 to 1.14 ppm (r= 0.998, n=8). The method offers a detection limit of 0.025 ppm. The limit detection was 0.005 ppm.

The recovery of BPA was evaluated taking an aliquot of 1.0 ml of river water spiked to 4.57 ppm of BPA transferred to a voltammetric cell containing 9.0 mL of B-R buffer pH 8. The sample was analyzed by standard addition method. Mean recoveries for the samples were found to be between 95.8 % and 100.7 % (3 repetitions). The obtained value for the relative standard deviation was 2.43 %. The results were analyzed by applying Student´s test, the experimental value did not exceed the theoretical value for the electroanalytical method, confirming no significant difference between the added and found value. The method was checked by HPLC and the results are in agreement. Therefore, the statistic values obtained are acceptable and suggest that the proposed procedure could be successful applied to the quantification of BPA in samples of river waters.

*Acknowledgement: Capes, Fapesp and CNPq.*

REFERENCES

1. Krishman A. V., Stathis P., Permuth S. F., Tokes L., Freldman D.: Endocrinology *132*, 2270 (1993).
2. Sajiki J., Yonekubo J.: Environ. Int. *30*, 145 (2004).
3. Kuramitz H., Nakata Y., Kawasaki M., Tanaka S.: Chemosphere *45*, 37 (2001).

## OP07

## FLOW-THROUGH CHRONOPOTENTIOMETRY IN PROCESS ANALYTICAL CHEMISTRY

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In process analytical chemistry rugged but sufficiently reliable methods are preferred. The intrinsic simplicity and high versatility of electroanalytical methods makes them interesting for unattended monitoring of electrochemically active species in industrial processes[1], waste water treatment plants and drinking water production.

The paper presents some innovative approaches to the long-term monitoring of river water for traces of Hg, Ni, Cd and Cr(VI)[2], waste waters from microelectronics for As, Pb, Sn and EDTA, cooling water for hydrazine, drinking water production for disinfection byproducts such as chlorites and bromates. All applications utilize flow-through electrochemical measurement either in chronopotentiometric or coulometric mode employing a simple flow-through electrochemical cell with long-lifetime working electrodes. The microprocessor controlled flow system combines the advantages of sequential and flow injection protocols, enabling virtually any kind of sample pre-treatment, even *in-situ* reagent preparation, automatic measurement of the blank, standard and samples. In most applications the electrochemical system is operating unattendedly for several weeks.

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REFERENCES

1. Beinrohr E., Dzurov J., Annus J., Broekaert J. A. C.: Fresenius' J. Anal. Chem. *201*, 362 (1998).
2. Manova A., Humenikova S., Strelec M., Beinrohr E.: Microchim. Acta *159*, 41 (2007).

## OP08

## HAEM PROTEINS IN NON-AQUEOUS SOLVENTS: ELECTROCHEMISTRY, STRUCTURE AND CATALYSIS

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The factors controlling the redox potential, $E^o$, of proteins and enzymes are of particular importance in investigating their biological function. The realisation that proteins can function in non-aqueous solvents has also widened their potential applications in biosensing and biocatalysis and in turn, has generated an interest in the effect of solvent on protein behaviour. It is important therefore to gain an understanding of how protein properties, such as redox potential and electron transfer kinetics, are affected by solvent composition. We are examining the electrochemical and biocatalytical properties of hemin[1], microperoxidase-11 (ref.[2]), myoglobin, haemoglobin[3], cytochrome c (ref.[4]), horseradish peroxidise[1] and chloroperoxidase in non-aqueous solvents with a view to using these proteins as biosensors and biocatalysts in non-aqueous solvents.

The enthalpy and entropy of cytochrome c reduction (on a self assembled monolayer (SAM) Au electrode) ranged from −54.4 to −18.1 kJ mol$^{-1}$ and −114.9 to 55.8 J K$^{-1}$ mol$^{-1}$, respectively in alcohol solutions. Similar results were obtained in other solvents. The SAM electrodes enable the examination of both spectroscopic (UV-Visible, resonance Raman and circular dichroism) and electrochemical properties. With proteins where the haem is not covalently attached to the peptide, it is likely that the haem is extracted to varying extents from the binding pocket. The thermodynamics of reduction of the haem moiety of hemin, microperoxidase-11, cytochrome c, myoglobin, haemoglobin and horseradish peroxidase in a range of solvents indicates that each protein and each solvent has to be examined independently, with no discernible trends evident between solvents.

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REFERENCES
1. Brusova Z., Gorton L., Magner E.: Langmuir *22*, 11453 (2006).
2. O' Donoghue D., Magner E.: Electrochim. Acta. *53*, 1134 (2007).
3. Ivanova E., Magner E.: Electrochem. Comm. *7*, 323 (2005).
4. O'Reilly N.J., Magner E.: Langmuir *21*, 1009 (2005).

## OP09

## SMOOTH AND MESOPOROUS Pt MICROELECTRODES MODIFIED BY UPD Bi FOR THE DETECTION OF TRACE METALS AND SMALL ORGANIC MOLECULES

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In recent years, bismuth film electrodes (BiFE's) have been proposed as an alternative to mercury-based electrodes for a variety of analytical applications, especially in stripping voltammetry (SV). The analytical performance of BiFE's, prepared both by *in-situ* and *ex-situ* electroplating of metallic bismuth onto appropriate electrode substrates, in analogy with the corresponding procedures of mercury deposition on solid materials, has been investigated in a number of papers. In particular, a variety of carbon electrodes of conventional size, such as glassy carbon or carbon paste, or microelectrodes such as carbon fibers and gold micodisks have been employed as substrates for the *in-situ* bismuth-film formation. *Ex-situ* plating of the bismuth-film onto glassy-carbon or bare carbon paste, as well as on screen-printed carbon electrodes has also been tested. The *ex-situ* prepared BiFE's offer a distinct advantage, as the addition of Bi(III) salts in the investigated medium is avoided. However, BiFE's thus fabricated require adequate physical and chemical stability, as they have to be transferred from the preparation/modification solution to the measuring cell device, and usually need to exhibit enhanced stability for multiple measurements. Moreover, the rather negative oxidation potential of metallic bismuth poses serious limitation for their use in the anodic range.

Metallic bismuth can also be deposited in a rather precise and controlled manner by exploiting the under potential deposition phenomenon (UPD). In this case, the electrodeposition of submonolayer to monolayer amounts of an adsorbate material on an electrode surface occurs at potentials positive to the bulk deposition potential. This in principle would allow the extension of the potential window to more positive values, and species such as copper could also be detected by ASV.

Bi atoms spontaneously and irreversibly adsorb onto the surface of platinum electrodes, and the adatoms remain adsorbed on the substrate surface even in media lacking their soluble species. This procedure can therefore be employed for the *ex-situ* fabrication of stable BiFE's, which can then be used for electroanalytical measurements.

In this paper, we report on the performance of either smooth or mesoporous platinum microdisk electrodes modified with submonolayers of adsorbed bismuth for ASV analysis of trace metals and small organic molecule determination. The mesoporous platinum films were electrodeposited from hexachloroplatinic acid dissolved in the aqueous domain of the lyotropic liquid crystalline phase of Brij 78®, to form metal films with hexagonal arrays of nanometer-sized channels.

## OP10

## ELECTROANALYSIS WITH NANOELECTRODE ENSEMBLES IN ROOM TEMPERATURE IONIC LIQUID

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Nanoelectrode ensembles (NEEs) are fabricated by growing metal nanowires in the pores of a template, typically a polycarbonate track-etched membrane. NEEs can exhibit three distinct voltammetric response regimes depending on the thickness of the diffusion layer and distance between the nanoelectrode elements; they are: a) total overlap regime: when radial diffusion boundary layers overlap totally (slow scan rates and/or small distance between nanoelectrodes); b) pure radial: when the nanoelectrodes behave independently under a radial diffusion regime (higher scan rates, larger distances between nanoelectrodes; c) linear active: when the nanoelectrodes behave as isolated planar electrodes (very high scan rates). The diffusion regime usually observed at NEEs fabricated from commercial track-etched membranes is the total overlap regime[1].

Really, for electroanalytical applications, the most advantageous regimes are the total overlap and the pure radial regimes since they give high faradaic-to-capacitive current ratios For instance, detection limits at NEEs in the total overlap regime are 2–3 orders of magnitude lower than at regular electrodes[2]. Notwithstanding these interesting analytical characteristics[3], NEEs application suffer for some limits that are: a) narrow potential window accessible; b) accessibility, with commercial membranes, only of the total overlap diffusive regime.

Recently, a large interest in a new kind of electrolytes, named room temperature ionic liquids (RTIL) showed interesting properties for electrochemical and electroanalytical application. Goal of the present research is to study the use of NEEs in RTILs, examining possible advantages coming from the widening of the accessible potential window as well as for the application of NEEs to analysis of organic molecules which are insoluble in water.

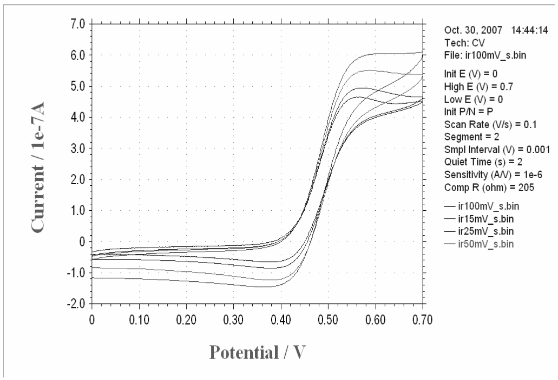

Fig. 1. **Cyclic voltammograms recorded at different scan rates** (from 15 to 100 mV $s^{-1}$) at NEE in $10^{-3}$ M ferrocene, BmIm($N(Tf)_2$) solution

A characteristic of ionic liquids which plays an important role to this respect is their viscosity. Typically, viscosities of RTILs are quite high. In the case of NEEs, we show that the increased viscosity determines the change of the diffusive regime from total overlap to radial. This was observed for different RTILs such as 1-Butyl-3-Methylimidazolium or 1-Butyl-1-Methyl-pyrrolidinium salts with tetrafluoborate, dicyanamide or bis(trifluoro-methylsulfonyl) imide anions.

Finally, we will discuss the role of RTIL on the analytical performances of NEEs, in particular in relation to detection limits and sensitivities for the analyses of water insoluble analytes, such as some vitamins.

REFERENCES
1. Menon V., Martin C. R.: Anal. Chem. *67*, 1920 (1995).
2. Ugo P., Moretto L. M., Vezzà F.: ChemPhysChem *3*, 917 (2002).
3. Moretto L. M., Pepe N., Ugo P.: Talanta *62*, 1055 (2004).

## OP11
## MAGNETIC NANOPARTICALS PLAY AN IMPORTANT ROLE IN ELECTROANALYTICAL CHEMISTRY

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Bifunctional nanoarchitecture has been developed by combining the magnetic iron oxide and the luminescent Ru$(bpy)_3^{2+}$ encapsulated in silica. Highly luminescent $Ru(bpy)_3^{2+}$ acts as an effective ECL reagent, while the magnetic $Fe_3O_4$ nanoparticals allow external manipulation through a magnetic field. On the basis of their unique characteristics, we fabricate a novel ECL sensor possessing excellent performance. On the other hand, a simple sonicating method for rapid synthesis of ECL sensor material with gold nanoparticals supported on $Ru(bpy)_3^{2+}$ doped silica / $Fe_3O_4$ nanocomposite is presented. Such bifunctional nanoparticals also have great potential in combination with ECL detection in bioanalysis.

A new kind of electrochemical sensor with $Fe_3O_4$ NPs as an artificial enzyme to detect $H_2O_2$ is proposed. The detection limit of the prepared sensor is as low as 1.6 μM. Notably, the sensor shows distinguished stability; it could maintain 92.3 % of its initial response after 50-day storage under room temperature. Moreover, possessing both magnetic property and electrocatalytic capability, $Fe_3O_4$ NPs could also be effectively used in magnetic separation and electrochemical detection of biomolecules.

*Financial support from NSFC is greatly appreciated.*

## OP12
## ELECTROCHEMICALSENSORS BASED ON ORGANIC ELECTROCHEMICAL TRANSISTORS

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Conjugated polymers are useful both as transducers and sensing membranes in several types of electrochemical sensors including potentiometric, amperometric and conductimetric sensors, as well as chemically sensitive field effect transistors[1]. The recent developments of electrochemical transistors based on poly(3,4-ethylenedioxythiophene) doped with poly (styrenesulfonate) (PEDOT/PSS) in the form of lateral architectures offer additional possibilities for fabrication of electrochemical sensors[2,3]. The working principal of the electrochemical transistor is based on reversible electrochemical oxidation/reduction of PEDOT/PSS with simultaneous cation transfer from/to the PEDOT/PSS film. Consequently, the transistor response depends on the presence of cations in the medium in which the transistor is immersed. Selectivity can be obtained by coating the PEDOT/PSS layer with a sensing membrane[3]. In this work, different ion-selective outer mem-

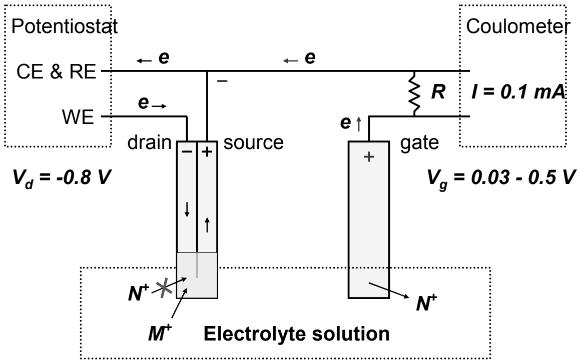

Fig. 1. **Experimental set-up for the measurement**

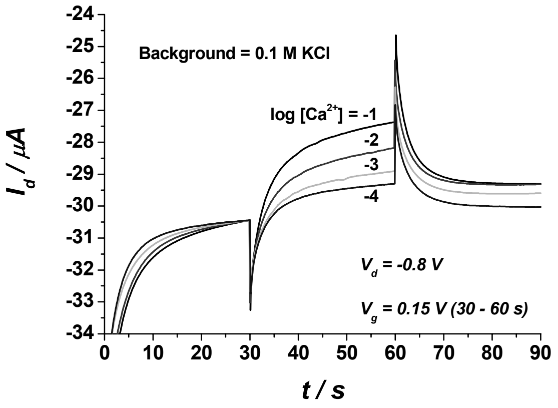

Fig. 2. **Transistor response on changes in [$Ca^{2+}$] in the sample solution**

branes are deposited on top of the PEDOT/PSS-based electrochemical transistor in order to evaluate the possibilities of achieving novel electrochemical sensors based on organic electrochemical transistors[4].

The experimental set-up is shown Fig. 1. The electrochemical transistor was tested by placing a calcium selective membrane on the PEDOT/PSS substrate (lower end of the right electrode in Fig. 1) and immersing it in a solution of calcium ions. The parameters of the transistor for optimal response were first studied. The test solution was 0.1 M KCl and 0.1 M $CaCl_2$. The drain voltage was kept constant at –0.8 V but the gate voltage was varied between 0.03 and 0.5 V. The current between drain and source was measured as the response signal and was monitored during 60 s after the gate voltage was applied. The optimal response was obtained at the gate voltage of 0.15 V. When the concentration of calcium was changed between 0.1 M and 0.1 mM in the 0.1 M KCl background solution the responses shown in Fig. 2 were obtained. As can be seen in that figure the drain current was found to depend on the concentration of calcium ions in the test solution.

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REFERENCES

1. Bobacka J., in: *Encyclopedia of Sensors*. (Grimes C. A., Dickey E. C., Pishko M. V., ed.), Vol. 2, p. 279. American Scientific Publishers 2006.
2. Nilsson D., Chen M., Kugler T., Remonen T., Armgarth M., Berggren M.: Adv. Mater *14*, 51 (2002).
3. Nilsson D., Kugler T., Svensson P.-O., Berggren M.: Sens. Actuators, B *86*, 193 (2002).
4. Berggren M., Forchheimer R., Bobacka J., Svensson P.-O., Nilsson D., Larsson O., Ivaska A.: in Bernards

## OP13

## MONITORING HEAVY METALS IN SEAWATER BY ELECTROCHEMICALLY INDUCED DEPOSITION AS HYDROXIDES

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Electrochemical co-deposition of various metal hydroxides, driven by the change of pH at the surface of a gold electrode, is the basis of a novel method for monitoring heavy metals in seawater. All metals, regardless of their electroactivity, can be deposited as hydroxides, and the process may be manipulated by controlling the current density. Application of a negative potential or current produces hydroxyl ions from water, thereby elevating the pH, causing metals to co-precipitate with $Mg(OH)_2$. Continuous deposition enriches the precipitate with the metals, which are then determined by ICP-MS, upon dissolution of the deposit. One measurement furnishes information regarding the pollution of the tested water and determines several metals simultaneously. Metals present in seawater in very low concentrations (below detection limit of most analytical instruments), may be quantified by prolonging the duration of the precipitation. Spiking of seawater with 1–10 ppm of Cu, Cr, Co, Zn and Pb, caused the metals to accumulate in the precipitate as a function of time and concentration in seawater. Analysis of the precipitates by SEM, EDS and XPS, indicated that the metal hydroxides formed a separate phase from $Mg(OH)_2$ and even water electro-reducible metals, e.g., $Cu^{2+}$, preferentially precipitated as hydroxides. Distribution constants correlating the concentrations of the metals in the deposited salts to their concentrations in seawater were calculated. These calculations imply that the mechanism governing the precipitation of the metal hydroxides by the electrochemically induced process is likely to be kinetically and mass-transport driven, rather than thermodynamically controlled.

## OP14

## LABEL-FREE ELECTRICAL DETECTION OF PROTEIN INTERACTIONS WITH PEPTIDE APTAMERS

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The study of protein interactions is a fast expanding field where present detection technologies have thus far failed to have a strong presence. Label-free electrical detection techniques suitable for protein microarrays are therefore highly desirable. Field-effect devices, such as those previously developed for DNA sensing[1], are promising candidates for the development of inexpensive microarrays associated with portable instrumentation. These stable semiconductor devices measure variations in the open circuit potential (OCP) that occur at the metal gate interface when the charge density and distribution of the immobilised biolayer changes upon interaction with a bioconjugate.

We here report on the electrical detection of protein interactions relevant to cancer research applications. Peptide aptamers that mimic specific protein interactions[2] were immobilised on Au electrodes and their interaction with cyclindependent protein kinases (CDK) was detected by direct measurement of variations in OCP. The OCP was measured in real-time using an ultra-low input bias current instrumentation amplifier providing an accurate differential measurement of voltage. Different peptide aptamers were used for the successful detection of CDK2 and CDK4 in yeast lysates. Variations of the OCP with the pH of the measurement buffer confirm that the effects observed correspond to variations in charge upon protein interaction.

The density of the immobilised peptide aptamers and the efficiency of their interactions with CDK lysates were checked by quartz crystal microbalance measurements. Variations in charge transfer resistance and in protein/double-layer capacitance measured by electrochemical impedance spectroscopy with charged redox markers in solution are in agreement with the OCP measurements.

The present work shows that label-free electrical detection of protein interactions with peptide aptamers can be achieved either by direct detection of the OCP with suitable instrumentation or in conjunction with field-effect transistors, where similar potential shifts were also observed.

REFERENCES

1. Estrela P., Migliorato P.: J. Mater. Chem. *17*, 219 (2007).
2. Woodman R., Yeh J. T. H., Laurenson S., Ko Ferrigno P.: J. Mol. Biol. *352*, 1118 (2005).

## OP15

## *N*-NITROSOAMINES AS REAGENTS FOR THE CONTROLLED RELEASE OF NITRIC OXIDE VIA DISSOCIATIVE ELECTRON TRANSFER

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Of the methods that have been previously employed for the observation of cellular chemokinesis or chemotaxis by chemicals, the most conceptually exciting for both qualitative and quantitative measurements involves the use of a dual electrode system in a collector-generator mode. This electrochemical technique exquisitely exploits the advantages and superiority of electrochemical methods in yielding dynamic and qualitative information on systems in real time. Consequently, in order to capitalise on this technology, electrolytic methods for the synthesis of bio-signalling molecules need to be established. Dissociative electron transfer (the cleavage of a $\sigma$-bond due to electron transfer between the electrode and a redox active species) is seen as an elegant, chemically clean and mild method to achieve this. In this work, the heterogeneous dissociative electron transfer of *N*-nitrosoamines is considered as a means for nitric oxide generation from a variety of precursors. Further, in order to implement these systems as a source of nitric oxide, it is pertinent to ascertain whether electron transfer initiated release follows a concerted or stepwise pathway. This will be addressed, together with the use of *N*-nitrosoamines not only as sources of nitric oxide, but also as useful and alternative reagents for the electro-grafting of a species to an electrode.

*The authors thank the EPSRC and the University of Hull for funding.*

## OP16

## CONSTRUCTION OF ELECTROCHEMICALLY LABELED OLIGONUCLEOTIDES AND THEIR USE IN ANALYSIS OF NUCLEOTIDE SEQUENCES AND PROBING OF DNA-PROTEIN INTERACTIONS

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Labeling of nucleic acids (NA) with electrochemically active groups is utilized to increase the selectivity and sensitivity of the NA electrochemical detection. Although the NA are electrochemically active themselves[1], attaching an electroactive tag to a specific nucleotide sequence helps one to recognize it among other nucleotide sequences. Besides techniques of solid-phase chemical synthesis of oligonucleotides (ON), the electroactive labels can be introduced into the ON via post-synthetic chemical modification (e.g., with osmium tetroxide complexes, Os,L[2]) or via enzymatic incorporation of labeled nucleotides[3,4].

The Os,L react selectively with thymine residue in single-stranded DNA under physiological conditions, forming covalent electroactive adducts. ON probes modified with Os,L bearing different ligands (L) differ in their peak potentials which has been utilized in electrochemical "multicolor" DNA sensing[2]. Deoxynucleoside triphosphate (dNTP) conjugates with various electroactive moieties (such as ferrocene[3], amino or nitro phenyl groups[4]), attached to the nucleobase, have been prepared via aqueous-phase cross-coupling reactions. These dNTP can easily be incorporated in ON sequence-specifically by primer extension. Due to electronic conjugation via unsaturated (ethinyl) bridge, electrochemical properties of these labels depend on the coupled nucleobase and respond to incorporation into DNA. We have applied this labeling strategy, in connection with magnetoseparation techniques[1], for the detection of single nucleotide polymorphisms, probing abundance of a specific nucleobase in a target DNA stretch, as well as in monitoring of DNA-protein interactions.

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REFERENCES

1. Palecek E., Fojta M.: Talanta *74*, 276 (2007).
2. Fojta M., Kostecka P., Trefulka M., Havran L., Palecek E.: Anal. Chem. *79*, 1022 (2007).
3. Brazdilova P., Vrabel M., Pohl R., Pivonkova H., Havran L., Hocek M., Fojta M.: Chem-Eur. J. *13*, 9527 (2007).
4. Cahova H., Havran L., Brazdilova P., Pivonkova H., Pohl R., Fojta M., Hocek M.: Angew. Chem. Int. Ed., in press.

## OP17

## DIFFERENTIAL ELECTROLYTIC POTENTIOMETRIC, A DETECTOR FOR FIA DETERMINATION OF VITAMIN C IN PHARMACEUTICAL PREPARATIONS

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Many methods have been reported in comprehensive reviews for the determination of ascorbic acid[1–5]. These methods include spectrophotometric methods using reagents such as dichlorophenolindophenol[6] Eriochromecyamine[7], Fast Blue Salt-B (ref.[8]), silicon molybdenum heteropoly blue (ref.[9]), copper sulphate in the presence of neocuprine (ref.[10]), *etc.* Chromatographic techniques such as HPLC with electrochemical detection (ref.[11]), liquid chromatography with electrochemical detection (ref.[12]), ion-suppression reverse phase chromatography (ref.[13]), capillary zone electrophoresis (ref.[14]), *etc.* have also been applied for ascorbic acid assay. A number of different types of voltammetric methods making use of a variety of electrodes have also been developed[15–18]. Most of the methods developed for ascorbic acid are visual and potentiometric titrants such as ceric ammonium sulphate[19], *N*-chlorosuccinimide[20], peroxymono sulphate[21], hexacyanoferrate(III) (ref.[22]), mercury(II) nitrate (ref.[23]), silver nitrate (ref.[24]), copper(II) sulphate (ref.[25]), codine[26] and *N* bromosuccinimide (ref.[27]). The widely used British Pharmacopoeia (BP) method recommends visual titration of ascorbic acid[28] with cerium(IV) (ref.[29]). Visual titrimetric methods cannot be applied successfully for the ascorbic acid assay in coloured and opaque pharmaceutical solutions and also require large sample size.

The technique of direct current differential electrolytic potentiometry (d.c.DEP) consists of polarizing two identical electrodes with a stabilized small current and measuring the potential differences between them. The d.c.DEP technique has been applied to various types of titrimetric reactions in both aqueous[30–33] and non-aqueous media[34–38] sing different types of electrodes. Using this technique the polarized electrodes respond faster, the apparatus is simple and the salt bridge problems of the reference cell are eliminated. This paper describes oxidation reaction where vitamin C is being oxidized with Ce (IV).

Differential electrolytic potentiometry (DEP) was coupled with Flow injection analysis (FIA) technique for the determination of ascorbic acid in pharmaceutical preparations.

Platinum electrodes were used as an indicating system to follow the oxidation of vitamin C with potassium iodate, and permanganate in an acidic medium. The oxidation reactions of vitamin C with Iodate and permanganate are fast enough to permit its determination by flow injection in sulfuric acid media. The univariate method was employed to optimize the variables such as the current density, the flow rate, the oxidant concentration and the concentration of sulfuric acid, the optimum conditions were found to be as follow: iodate concentration is 8.35 mM, permanganate concentration is 0.11 mM, current density is 40 $\mu$Acm$^{-2}$, and flow rate is 25 $\mu$lsec$^{-1}$.

The proposed method was linear in the range 18–36 $\mu$gml$^{-1}$ using permanganate, the DL and R$^2$ values were 11 $\mu$gml$^{-1}$ and 0.996 respectively. Using iodate as oxidant the range was 12–130 $\mu$gml$^{-1}$with DL and R$^2$ of 9 $\mu$gml$^{-1}$ and 0.999 respectively.

The procedure was applied successfully to the determination of vitamin C in commercial tablets. The results of this study were favorably compared statistically with those obtained with official methods.

REFERENCES

1. Hashmi M., in: *Assay of Vitamins in Pharamaceutical Preparations*, p. 286.Wiley-Interscience, New York 1972.
2. Al-Meshal I. A., Hussan M. A., in: *Analaytical Profiles of Drug Substances*, p. 45. (Florey K., ed.). Academic Press, New York 1982.
3. Augesten J., Kelein B. P., Becker O., Venugopal P., in: *Methods of Vitamin Assay*, p. 303. Wiley-Interscience, New York 1985.
4. Washko P. W., Welch R. W., Dharwal K. R., Wang Y., Levine M.: Anal. Biochem. *204*, 1 (1992).
5. Fatibello Fo O., Dos Santos A. J. M. G.: Talanta *40*, 593 (1993).
6. Davies S. H. R., Masten S. J.: Anal. Chim. Acta *248*, 225 (1991).
7. Kania K., Bhal F.: Chem. Anal. (Warsaw) *35*, 775 (1990).
8. Zang W. D., Huang H. G.: Fenxi Huaxue *21*, 597 (1993).
9. Li G., Yu R.: Henliang Fenxi *9*, 79 (1993).
10. Farooqui M. I., Anwar J. M., Abdullah A., Rozina M., Mahood R.: J. Chem. Soc. Pak. *12*, 333 (1990).
11. Iwase H., Ono I.: J. Chromatogr. *654*, 215 (1993).
12. Nagy E., Degrtell I.: J. Chromatogr. Biomed. Anal. *89*, 276 (1989).
13. Kenneddy J. F., White C. A.: Food Chem. *28*, 257 (1988).
14. Lin Ling B., Bxeyen W. R. G., Van Aeler P., Dewalle P.: J. Pharm. Biomed. Anal. *10*, 717 (1992).
15. Marian I. O., Sandulescu R., Bonciocat N.: J. Pharm. Biomed. Anal., *23*, 227 (2000).

16. Sandulescu R., Mirel S., Oprean R.: J. Pharm. Biomed. Anal. *23*, 77 (2000).
17. Cai C. X., Xue K. H. : Microchem. J. *61*, 183 (1999).
18. Shankaran D. R., Narayanan S. S.: Fresenius' J. Anal. Chem. *364*, 686 (1999).
19. Al-Rikabi A. M. K., Al-Jabri F. M., Al-Motheer T. M.: Anal. Lett. *23*, 273 (1990).
20. Gupta A., Bindra S., Sing Sunil S. K.: Mickrochim. Acta *3*, 81 (1989).
21. Riyazuddin P., Ali Mansoor S., Vasanthi R.: Bull. Electrochem. *4*, 295 (1988).
22. Peng W. F., Seddon B. J., Zhang X. J., Zhou X. Y., Zhao Z. F.: Fenxi Huaxue *20*, 838 (1992).
23. Ismail I. A., Khalifa H., Zaky M.: Microchem. J. *30*, 353 (1984).
24. Soliman R., Belal S. A.: Pharmazie *29*, 204 (1974).
25. Sichko A. I., Skrebtsova N. A.: Otkrytiya Izobret *5*, 123 (1991).
26. Petho G.: Pharm. Hung. *52*, 228 (1982).
27. Channu B. C. J., Kalpana H. N., Ramesh L., Eregowda G. B., Dass C., Thimmaiah K. N.: Anal. Sci. *16*, 859 (2000).
28. Bristish Pharmacopoeia, Vol. II, HMSO, London, 1980, p. 733.
29. Bristish Pharmacopoeia, Vol. I, HMSO, London, 1980, p. 39.
30. Abdennabi A. M. S., Koken M. E.: Talanta *46*, 639 (1998).
31. Abulkibash A. M. S., Koken M. E., Khaled M. M., Sultan S. M.: Talanta *52*, 1139 (2000).
32. Abulkibash A. M. S., Sultan S. M., Al-Olyan A. M., Al-Ghannam S. M.: Talanta *61*, 239 (2003).
33. Al-Ghannam S. M.: Il Farmaco *59*, 331 (2004).
34. Abulkibash A. M. S., Al-Ghannam S. M., Al-Olyan A. M.: J. AOAC Int. *87*, 671 (2004).
35. Abdennabi A. M. S., Bishop E.: Analyst *107*, 1032 (1982).
36. Bishop E., Abdennabi A. M. S.: Analyst *108*, 1349 (1983).
37. Abdennabi A. M. S., Bishop E.: Analyst *108*, 71 (1983).
38. Abdennabi A. M. S., Bishop E.: Analyst *108*, 1227 (1983).

## OP18

## NOVEL APPROACHES IN THE DEVELOPMENT OF AMPEROMETRIC IMMUNOSENSORS FOR THE DETERMINATION OF *Staphylococcus aureus*: PEROXIDASE-LABELLED SYSTEMS BASED ON DTSP-MODIFIED GOLD ELECTRODES

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In this work, the development of two amperometric immunosensors based on covalent immobilization of RbIgG onto a DTSP self-assembled monolayer for *Staphylococcus aureus* determination is described. The difference between the two configurations is that one of them uses antiRbIgG-HRP as enzyme marker and the other one uses protein A-HRP. Both immunosensors are based on a competitive format which involves competition between S. aureus cells and the enzyme-labelled reagent for the binding sites of RbIgG covalently immobilized onto the electrode surface. Tetrathiafulvalene (TTF) was used as redox mediator in the $H_2O_2$ reduction process catalyzed by HRP, and was entrapped at the electrode surface by cross-linking with glutaraldehyde[1].

The sensor fabricated with antiRbIgG-HRP gave the best analytical characteristics with a limit of detection of $3.42\times10^5$ cells mL$^{-1}$. The repeatability of the measurements with the same immunosensor and the reproducibility of the responses obtained with different immunosensors were 7.3 % and 9.1 % respectively.

In order to improve sensitivity cells wall lysis was assayed using two procedures: heat and ultrasonic treatments. These processes produced the breaking of bacteria and the availability of many more protein A-bearing cell portions[2]. In the most favourable experimental conditions, after cell wall lyses by ultrasonic treatment, a decrease of one order of magnitude in the detection limit was achieved, now being possible to detect $1.25\times10^4$ cells mL$^{-1}$.

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REFERENCES

1. Campuzano S., Pedrero M., Pingarrón J. M.: Talanta *66*, 1310 (2005).
2. Taylor A. D., Yu Q., Chen S., Homola J., Jiang S.: Sens. Actuators, B *107*, 202 (2005).

## OP19

## APTASENSORS FOR SMALL MOLECULES: A COMPETITIVE IMPEDIMETRIC ASSAY FOR THE DETECTION OF AMINOGLYCOSIDE ANTIBIOTICS

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Aminoglycoside are broad spectrum antibiotics with bactericide activity against some Gram positive and many Gram negative organisms. Given that most of them cause severe secondary effects such as ototoxicity and nephrotoxicity a precise control of the dose and the pharmacokinetics is required. Detection of aminoglycoside antibiotics is a challenging problem because they lack useful spectroscopic and electrochemical features. Time-consuming label-based immunoassays, electrophoretic and HPLC methods with derivatization reactions have been proposed for the detection of tobramycin and neomycin B[1].

Aptamers are short synthetic DNA or RNA oligonucleotides that fold into multiple conformations to form a binding pocket to interact with a great variety of ligands with high affinity and specificity. Their excellent chemical and thermal stability as well as their resistance to iterative cycles of denaturation make aptamers a very promising recognition molecule for sensing.

However, the detection of small molecules using aptamers is still challenging. Here, we present a general protocol for the determination of small molecules such as antibiotics by faradaic impedance spectroscopy (FIS)[2]. A competitive assay format is proposed in which the free aminoglycoside in solution displaces the aptamer from its complex with a surface-bound aminoglycoside, diminishing the electron transfer resistance. A nuclease-resistance RNA aptamer is used to ensure their applicability to biological fluids. The analytical characteristics of the device as well as the kinetics of the aptamer-aminoglycoside interaction using surface plasmon resonance spectroscopy (SPR) analysis are studied.

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REFERENCES

1. Stead D. A.: J. Chromatogr., B *747*, 69 (2000).
2. de-los-Santos-Alvarez N., Lobo-Castañón M. J., Miranda-Ordieres A. J., Tuñón-Blanco P. J.: Am. Chem. Soc. *129*, 3808 (2007).

## OP20

## BIOSENSORS AND BIOFUEL CELL ANODES BASED ON NEW SUGAR OXIDISING REDOX ENZYMES

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A number of new sugar oxidising redox enzymes and variants thereof, *viz.* pyranose dehydrogenase (PDH), pyranose oxidase (P2O), and cellobiose dehydrogenase (CDH) have recently been electrochemically characterised for use in biosensors for sugar or catecholamine detection but lately also for possible use in biofuel cell anodes. These redox enzymes come from different white and/or brown rot fungi and contain strongly bound FAD in the active site. CDH additionally also contains a cytochrome *b*. Electron transfer between these enzymes and electrodes can easily be obtained through different mediated approaches using 2 $e^-$ $H^+$ acceptors (e.g. soluble quinines) or 1 $e^-$ acceptors (e.g., $Os^{2+/3+}$-complex containing flexible polymers)[1,2]. Additionally due to its cytochrome *b* domain CDH shows very facile direct electron transfer characteristics with electrodes making third generation biosensors possible[3]. CDH similarly to glucose oxidase oxidises the sugar on the C1 carbon making it anomeric sensitive and is selective for the β-form. Depending on the origin white rot CDH is selective for lactose and cellodextrins[3], whereas brown rot CDH also efficiently oxidises both monosaccharides and other disaccharides[2]. In contrast PDH and P2O oxidise the sugar on the C2 or C3 carbon (or on both) making them anomeric insensitive. Both PDH and P2O are highly unselective and PDH even oxidises sucrose with a high turn over rate[1]. Additionally especially for PDH there is a possibility that the oxidation product is in turn also a substrate and for some PDHs a sugar molecule can be oxidised up to three times and is thus a very valuable redox enzyme for biofuel cell studies.

These enzymes can also be used for amplified detection of catecholamines and similar compounds. At the enzyme modified electrode a catecholamine is initially oxidised into its quinone counterpart and is thus transformed into an active form that can work as a mediator between the reduced enzyme active site and the electrode. Thus an amplification cycle is formed and detection limits in the subpicomolar range can be obtained[4].

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REFERENCES

1. Tasca F., Timur S., Ludwig R., Haltrich D., Volc J., Antiochia R., Gorton L.: Electroanalysis *19*, 194 (2007).
2. Harreither W., Coman V., Ludwig R., Haltrich D., Gorton L.: Electroanalysis *19*, 172 (2007).
3. Stoica L., Ludwig R., Haltrich D., Gorton L.: Anal. Chem. *78*, 393 (2006).
4. Stoica L., Lindgren-Sjölin A., Ruzgas T., Gorton L.: Anal. Chem. *76*, 4690 (2004).

## OP21

## CHARACTERISATION OF NEW CARBON FILM ELECTRODES FOR ELECTROCHEMICAL SENSORS

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The electrochemical, morphological and microstructural properties of carbon film electrodes made from carbon film electrical resistors of several different nominal resistances from 1.5 Ω up to 2 kΩ have been investigated before and after cycling in perchloric acid or electrochemical pre-treatment at +0.9 V *vs* SCE and integrated with previous studies on 2 Ω carbon film resistor electrodes[1,2]. Comparison has also been done with other types of carbon electrode, such as glassy carbon, carbon composite and at carbon films deposited on piezoelectric quartz crystals.

The electrochemical behaviour has been evaluated by cyclic voltammetry in buffer electrolytes to determine the kinetic parameters of model redox systems. The 1.5 Ω resistor electrodes show the best properties for sensor development with wide potential windows, and close-to-reversible kinetic parameters after electrochemical pre-treatment. Electrochemical impedance spectroscopy was used to relate these results to the interfacial properties of the electrodes. Microstructural and morphological studies were carried out using contact mode Atomic Force Microscopy (AFM) at the nanometre scale, Confocal Raman spectroscopy and X-ray diffraction, the latter demonstrating the existence of a graphitic structure with AFM evidencing the nanometric roughness. The effect of Nafion coatings, important for trace metal ion analysis in complex matrices, was also investigated as well as the usefulness of deposition of bismuth film electrodes under the Nafion coatings for extending the negative potential limit. It was found that best results for polymer-coated electrodes were obtained with 15 Ω carbon film resistors, possibly due to better adhesion on the rougher surfaces.

Future applications and perspectives will be discussed.

REFERENCES

1. Brett C. M. A., Angnes L., Liess H. D.: Electroanalysis *13*, 765 (2001).
2. Filipe O. M. S., Brett C. M. A.: Electroanalysis *16*, 994 (2004).

## OP22

## VOLTAMMETRIC CONTROL OF HOMEOSTASIS OF HUMAN METABOLISM

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One of the intermediates of human metabolic processes is thiodiglycolic acid (TDGA), formed by reaction between oxidation products of 2C units and derivatives of cysteine. It gets partly further oxidized and partly it dissolves in urine. Under normal conditions of metabolic homeostasis of healthy persons the concentration of TDGA in urine is less than 20 mg $L^{-1}$. It increases after exposure to xenobiotics[1], pharmaceuticals[2] or food components releasing 2C units, and after disturbance of metabolic redox equilibrium[3,4], e.g., by thio compounds, or by application of vitamin $B_{12}$. The TDGA concentration is hence a sensitive indicator of actual state of human metabolism. We worked out a simple and sensitive d.c. voltammetric method for TDGA determination in urine[1]: after elution of urine sample in a column of PVC powder, the protonated $-S-CH_2-$ bond of TDGA is reduced on the working electrode at about −1.0 V *vs.* SCE in an acid solution.

In our study of the effect of creatine supplementation on the physical output of sportsmen by analysis of TDGA in their urine[5,6], we found that the best physical fitness had the men in whose urine the TDGA increased least, and that the reactions of metabolisms of the 11 tested men showed different tendencies.

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REFERENCES

1. Dlaskova Z., Navratil T., Heyrovsky M., Pelclova D., Novotny L.: Anal. Bioanal. Chem. *375*, 164 (2003).
2. Navratil T., Senholdova-Dlaskova Z., Heyrovsky M., Pristoupilova K., Pristoupil T. I., Pelclova D.: Anal. Lett. *37*, 1093 (2004).
3. Pristoupilova K., Pristoupil T. I., Navratil T., Heyrovsky M., Senholdova Z., Pelclova D.: Anal. Lett. *38*, 613 (2005).
4. Navratil T., Petr M., Senholdova Z., Pristoupilova K., Pristoupil T. I., Heyrovsky M., Pelclova D., Kohlikova E.: Physiol. Res. *56*, 113 (2007).
5. Navratil T., Kohlikova E., Petr M., Heyrovsky M., Pelclova D., Pristoupilova K., Pristoupil T. I., Senholdova Z.: Food Chem., submitted.
6. Navratil T., Kohlikova E., Petr M., Heyrovsky M., Pelclova D., Pristoupilova K., Pristoupil T. I., Senholdova Z.: Food Chem., submitted.

## OP23

## ANTIMONY FILM ELECTRODE FOR ELECTROCHEMICAL STRIPPING MEASUREMENT OF TRACE HEAVY METALS

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Electrochemical stripping techniques still attract considerable attention for trace metal analysis and for measuring several important organic compounds, due to their unique capabilities of pre-concentrating the analytes at the electrode surface and associated favorable low limits of detection. Despite their well-known toxicity, mercury based electrodes have been used most commonly in the last five decades. In the year 2000, bismuth film electrode has been suggested as a suitable alternative for mercury analogue and has been, by now, accepted in many electroanalytical laboratories worldwide[1]. Recently, we presented antimony film electrode for anodic stripping analysis of trace heavy metals, which revealed attractive electroanalytical performance[2].

In this work, an early study of the antimony film electrode, as a suitable alternative "mercury-free" sensor for trace metal analysis, is presented. The antimony film electrode was employed in voltammetric and potentiometric stripping mode, in non-deaerated model solutions, in combination with different supporting electrodes, and several key operational parameters were examined and optimized. The SbFE exhibited excellent performance for measuring cadmium, lead, mercury, and bismuth as model metal ions, particularly under more acidic conditions with pH 2 or lower, and holds great promise for its broader application, e.g., in environmental and industrial monitoring.

REFERENCES

1. Wang J., Lu J. M., Hocevar S. B., Farias P. A. M., Ogorevc B.: Anal. Chem. *72*, 3218 (2000).
2. Hocevar S. B., Svancara I., Ogorevc B., Vytras K.: Anal. Chem. *79*, 8639 (2007).

## OP24
## URANIUM SORPTION ONTO SIDERITE IN CARBONATE MIXTURES

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Siderite, an iron (II) carbonate, is a compound of major interest for environmental issues. Present in natural geological formations, it can intervene as an agent able to remove pollutants (e.g. chromium[1], technetium[2]), by mechanisms mainly based on redox reactions. Despites the existence of groundwaters contaminated by uranium, because of mining or extraction processing, the reactivity of siderite towards this radionucleide has, to our knowledge, never been studied.

In order to investigate the complex mechanisms involved, we employ thin layers of siderite electrophoretically deposited on quartz covered by gold, which are used as modified electrodes in the interaction studies[3].

The siderite/uranium system was considered in carbonate solutions, for several pH and different carbonate total concentrations. The potential and the variation of mass at the surface of the working electrode were followed *in-situ* with an electrochemical quartz crystal microbalance. The study of the solution by alpha liquid scintillation was coupled with the one of the solid by cyclic voltametry and X-ray photoelectron spectroscopy. Thus, kinetics and mechanism of sorption can be proposed.

REFERENCES

1. Erdem M., Gür F., Tümen F.: J. Hazard. Mater. *B113*, 217 (2004).
2. Cui D., Eriksen T. E.: Environ. Sci. Technol. *30*, 2259 (1996).
3. Ithurbide A., Peulon S., Miserque F., Beaucaire C., Chausse A., Poinssot C.: Electrochim. Acta, submitted.

## OP25
## DISPOSABLE ELECTROCHEMICAL IMMUNOSENSORS FOR THE DETECTION OF BOLDANONE IN BOVINE URINE

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Selection of the appropriate electrochemical technique is a crucial requirement to facilitate the reduction of sample matrix effects in the development of biosensors. In the present work, a range of electrochemical techniques were studied and their performance in the detection of boldanone in bovine urine was compared. Chronoamperometry was found to be the most sensitive technique. A prototype device and PC software was developed to support the sensor development and the evaluation process (Fig. 1).

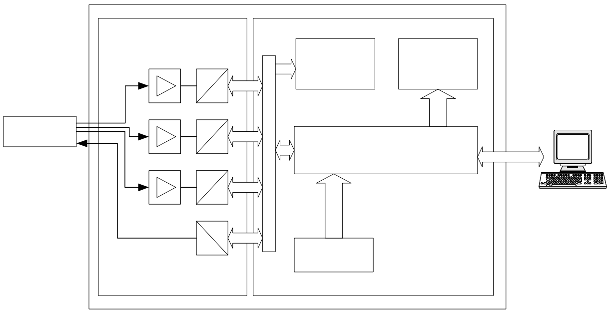

Fig. 1. **Schematic diagram of the measurement device**

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## OP26
## HETEROGENEOUS CARBON ELECTRODES

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Heterogeneous carbon electrodes are characterized by embedment of electrically conductive carbon particles (graphite, glassy carbon) in a liquid or solid matrix. The most prominent representatives are carbon paste (CPEs) and screen printed carbon electrodes (SPCEs). The heterogeneous nature of such materials facilitates their modification, in the simplest form just by direct addition of modifying agents ("direct mixing")[1–3].

Electrodes prepared from such materials can be well exploited for designing sensors with good analytical performance. Particular emphasis is paid to the development of biosensors, where a biological entity (e.g., enzyme) is involved in the recognition process of the sensor. Heterogeneous carbon materials (e.g., CPEs) are best suited for basic investigations of such systems due to their ease of modification under very moderate conditions. In case that they are mechanically more stable (e.g., SPCEs) mass production is possible.

Oxidases which produce hydrogen peroxide as by-product are of particular interest for developing electrochemical biosensors due to its electrochemical activity. Whereas direct oxidation and reduction requires unfavorably high positive or negative potentials due to overpotentials, metal oxides may be used as corresponding mediators.

Examples will be given with manganese dioxide, tin dioxide, iron oxides and platinum metal oxides acting as mediators in biosensors for glucose, glutamate, the toxin β-*N*-oxalyl-α,β-diaminopropionic acid (β-ODAP causing chronic poisoning, lathyrism), and the biogenic amine sarcosine.

REFERENCES
1. Kalcher K.: Electroanalysis *2*, 419 (1990).
2. Kalcher K., Wang J., Kauffmann J.-M., Svancara I., Vytras K., Neuhold C., Zhongping Y.: Electroanalysis *7*, 5 (1995).
3. Kalcher K., Švancara I., Metelka R., Vytras K., Walcarius A., in: *Encyclopedia of Sensors. Heterogeneous Carbon Electrochemical Sensors* (Grimes C. A., Dickey E. C., Pishko M. V., ed.), Vol. 4, p. 283. American Scientific Publishers 2006.

## OP27

## ACHIEVEMENT OF LIMITING PERFORMANCE CHARACTERISTICS OF THE ENZYMES IN DIRECT BIOELECTROCATALYSIS

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Bioelectrocatalysis is a phenomenon of acceleration of electrode reactions by the enzymes. Direct bioelectrocatalysis presumes the direct electron exchange between the enzyme active site and the electrode without any use of diffusion free mediators. The most important applications of bioelectrocatalysis are fuel cells and biosensors.

The direct bioelectrocatalysis by the enzymes hydrogenases responsible in nature for oxidation/evolution of molecular hydrogen was first shown by our group in early 80-s of the last century[1]. After immersion into $H_2$-saturated solution, the hydrogenase electrode reached the equilibrium hydrogen potential. At positive overvoltages the hydrogenase electrode generated high anodic current, which can be attributed only to hydrogen oxidation. Cathodic current at negative overvoltages has been proven to occur due to $H_2$ evolution.

However, the involvement of the enzymes in direct bioelectrocatalysis is highly dependent on the electrode support. In order to achieve proper orientation of enzyme molecules on the surface and to provide overlapping of the electrode and enzyme active site electron orbitals we used electroactive and conductive polymers. Indeed, electropolymerization of substituted pyrrols and anilines, as well as azines prior to immobilization dramatically improves current-potential characteristics of the resulting enzyme electrodes. Comparing the amount of hydrogenases on the electrode surface and their activity both in homogeneous kinetics and electrocatalysis, we claimed the achievement of limiting performance characteristics of the enzymes in bioelectrocatalysis[2].

Except for hydrogenases the phenomenon of acceleration of bioelectrocatalysis with the use of conductive and electroactive polymers will be shown for other oxidoreductases enzymes. The examples of using enzyme electrodes both as fuel electrodes in biofuel cells and as biosensors will be given.

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REFERENCES
1. Yaropolov A. I., Karyakin A. A., Varfolomeev S. D., Berezin, I. V.: Bioelectrochem. Bioenerget. *12*, 267 (1984).
2. Karyakin A. A., Morozov S. V., Voronin O. G., Zorin N. A., Karyakina E. E., Fateyev V. N., Cosnier S.: Angew. Chem., Int. Ed. Engl. *46*, 7244 (2007).

## OP28

## POLYANILINE NANOSTRUCTURES AND THEIR APPLICATIONS TO CHEMICAL SENSORS AND BIOSENSORS

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We present methods for the nanostructuring of conducting polymer, polyaniline (PANI) and their application to electrochemical sensing. Before electrochemical polymerization of aniline, the surface of each electrode was modified with polystyrene (PS) templates to form monolayer or multi-layer films. PS nanoparticles of different size have been used to investigate the behaviour of films with different nanodimensions The charge of the template particles has also been used to control the mechanism of PANI growth. On electrodes modified with negatively charged PS nanoparticles, PANI has been found to grow around the template particles to form PS-PANI core-shell nanostructures. When negatively charged PS templates were used, the electropolymerized PANI grew from the surface of the electrode into the interstitial spaces between the PS to form PANI-PS nanocomposites. Further structures can be derived by the dissolution of the PS template to form hollow spheres or porous films, respectively. Additionally, PANI films with multiple orders of micro- and nanostructure have been prepared to create highly nodular, “cauliflower-like” nanostructures with high surface area. The morphology of these films has been confirmed by scanning electron microscopy.

When at nanoscale, unique properties of conducting polymers, such as higher conductivity and more rapid discrete electrochemical switching processes, become possible and open the large variety of applications. We assessed them for any benefits in development of electrochemical and biosensing devices. Amperometric responses towards the catalytic reduction of hydrogen peroxide ($H_2O_2$) and nitrite ion, ($NO_2^-$) were analyzed to evaluate the sensing properties of all fabricated films. Immobilization of horseradish peroxidase as a model enzyme allowed us to obtain an efficient $H_2O_2$ biosensor. Enzyme-free sensors based on the electrocatalytic oxidation of β-nicotinamide adenine dinucleotide (NADH) have also been studied. The results obtained have been explained in terms of surface area and electrochemical properties of the nanostructured PANI films.

## OP29

## CHARGE TRANSFER RESISTANCE MODELLING FOR OPTIMIZATION OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY DNA DETECTION

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Electrochemical Impedance Spectroscopy (EIS) is a promising technique for DNA detection. Hybridization of target DNA to immobilized probes results in an increased negative charge, causing an increased charge transfer resistance $R_{ct}$ for the negatively charged ferri/ferrocyanide redox couple.

Optimization of the $R_{ct}$ change requires a detailed understanding of the detection mechanism. We report on a novel model for the $R_{ct}$ variation with DNA charge, in which $R_{ct}$ depends on the potential barrier in the immobilized DNA layer, $\varphi_B$. The surface redox concentration $c_s$ and resulting exchange current density $j_0$ vary with $\varphi_B$ and the redox molecule charge $z$ according to a Boltzmann factor: $c_s = c_0\exp(-ze\varphi_B/kT)$. $\varphi_B$ is calculated using 3D finite element solution of the Poisson-Boltzmann equation (Fig. 1 inset). $\varphi_B$ and $j_0$ vary across the electrode surface. The exchange current is determined by integration and $R_{ct}$ calculated.

The model is used to select conditions for optimum sensor response. Calculated $R_{ct}$ values show a super-linear relation with probe surface density (Fig. 1). This is in good agreement with experimental data. The model also predicts an $I^z$ dependence of $R_{ct}$ with the measurement ionic strength $I$.

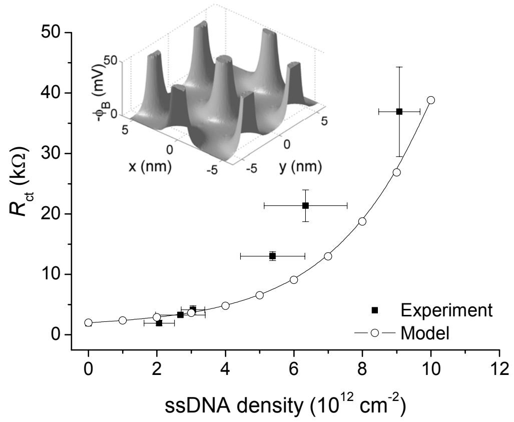

Fig. 1. **Comparison of experimental and calculated $R_{ct}$ variation with ssDNA probe density, for $I$ = 447 mM**. Error bars show the mean and spread of 3 samples. Inset: potential barrier for $3\times10^{12}$ cm$^{-2}$ ssDNA

The optimum probe density for maximum $R_{ct}$ change upon hybridization is a trade-off between charge screening and hybridization efficiency. At the high ionic strengths conventionally used for EIS DNA detection, high probe densities are required. The model predicts that reducing $I$ enables the use of lower probe densities where there is greater hybridization efficiency, significantly increasing the $R_{ct}$ change upon hybridization.

## OP30

## QUANTIFICATION OF ELECTROACTIVE MOLECULES USING A SERIAL DILUTION MICROFLUIDIC SYSTEM

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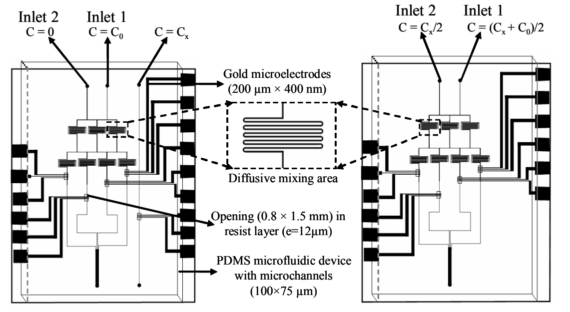
There is currently an increasing interest in the fields of microfluidics and lab-on-a-chip devices[1–3]. This analytical revolution is mainly driven by the possibilities of time and cost reduction associated with routine analysis while improving reproducibility and throughput (by employing many analytical cells in parallel). Moreover, portability and single-use are also advantages brought by these two concepts.

Electrochemical detection methods are more and more implemented on lab-on-a-chip devices due to their inherent ease of miniaturization, low power requirements, low limits of detection and compatibility with microfabrication technologies[4,5]. Moreover, electrochemistry presents a unique advantage compared to optical techniques (such as UV detection) that is the possibility of downsizing the detection window without loss of performance. Using electrochemical detection, it is possible to reach nM limits of detection[6] but also to carry out experiments *on-site* by using a portable device[7]. However, this detection technique presents also serious drawbacks that are inherent to the technique such as the need to have electroactive species and the fouling of the electrodes.

The determination of analyte concentrations can be achieved by various methods: *i*) calibration of a sensor, *ii*) addition of an internal reference in the sample and *iii*) successive additions of standard amount of analyte (standard addition method). The use of a calibration curve for the determination of an analyte concentration from a sensor signal is one of the more widely used procedure in analytical chemistry but this approach suffers from two main drawbacks. Indeed, the establishment of a calibration curve is *i*) a time consuming process requiring the preparation of various solutions, usually by manual dilutions and *ii*) the calibration curve needs to be re-evaluated regularly because of sensor deviation with time, for example.

The objective of this work was to design and characterize a microfluidic device that was able to perform amperometric qunatifications using an integrated calibration mode and an on-chip standard addition method. This microfluidic device (Fig. 1) can generate a calibration curve simultaneously to the sample analysis or can perform standard addition method by coupling a network of electrochemical sensors and a serial dilution microfluidic system. The serial dilution microstructure used in this work was already described elsewhere[8] and this type of structure (or similar type) was successfully implemented for different applications such as chemotaxis studies[9], cytotoxicity test, potentiometric titrations[10] and immunoassays[11]. During the presentation, we will describe briefly the elaboration of both microfluidic structure and electrode networks. Then, we will demonstrate their ability to carry out amperometric quantification of a model electroactive molecule using an integrated calibration mode and also a standard addition method.



Microfluidic titrator used in a calibration procedure

a

Microfluidic titrator used in a standard addition procedure

b

Fig. 1. **Schematic representation of the microfluidic structure made of PDMS that was used to quantify sample concentration using either an on-chip calibration curve (a) or a standard addition procedure (b)**. Each microchannel embedded in the PDMS slab was 100 µm wide and 80 µm deep. Electrode network on glass substrate featured 5 groups of 3-electrode electrochemical cells. (Note: diagrams are not drawn to scale)

*NanoLyon clean room facilities were used in this work to fabricate Au electrodes and microfluidic structures. S. K. is thankful to Region Rhône-Alpes for a MIRA PhD scholarship. This work was in part supported by Programme Interdisciplinaire CNRS – Interface Chimie Physique Biologie.*

REFERENCES

1. Dittrich P. S., Tachikawa K., Manz A.: Anal. Chem. *78*, 3887 (2006).
2. Szekely L., Guttman A.: Electrophoresis *26*, 4590 (2005).
3. Xu B., Du W., Liu B. F., Luo Q. M. : Curr. Anal. Chem. *2*, 67 (2006).
4. Nyholm L.: Analyst *130*, 599 (2005).
5. Pumera M., Merkoci A., Alegret S.: TRAC Trend. Anal. Chem. *25*, 219 (2006).
6. Vickers J. A., Henry C. S.: Electrophoresis *26*, 4641 (2005).
7. Kwakye S., Baeumner A.: Sens. Actuators, B *123*, 336 (2007).
8. Dertinger S. K. W., Chiu D. T., Jeon N. L., Whitesides G. M.: Anal. Chem. *73*, 1240 (2001).
9. Dertinger S. K. W., Jiang X., Li Z., Murthy V. N., Whitesides G. M.: Proc. Natl. Acad. Sci. U.S.A. *99*, 12542 (2002).
10. Ferrigno R., Lee J. N., Jiang X., Whitesides G. M.: Anal. Chem. *76*, 2273 (2004).
11. Jiang X., Ng J. M. K., Stroock A. D., Dertinger S. K. W., Whitesides G. M.: J. Am. Chem. Soc. *125*, 5294 (2003).

## OP31

## INTEGRATED BIOELECTROCATALYTIC SYSTEMS COMPOSED OF CARBON NANOTUBE-SUPPORTED MEDIATORS, ENZYMES AND METALLOPORHYRINS

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We have exploited here unique electronic and mechanical characteristics of multi-walled carbon nanotubes (MCNT) to construct the efficient anodic glucose oxidase based bioelectrocatalytic system. First, MCNTs have been modified with ultra-thin layers of tetrathiafulvalene (TTF) to form stable colloidal suspensions of carbon nanostructures. They have been utilized to produce Nafion-containing inks for sequential deposition of components. The presence of TTF is expected to facilitate an effective flow of electrons from the redox centers of glucose oxidase to the glassy carbon electrode. TTF and its derivatives constitute a group of redox molecules that were successfully used as redox mediators in the enzyme electrochemistry. As before, MCNTs have supported transport of electrons within the bio-electrocatalytic film. Our highly MCNT-based porous films have presumably acted as three-dimensional network of nanowires around the enzyme molecules and have promoted the efficient electron transfers. Thus we have produced a catalytic system capable of effective oxidation of glucose in 0.1 M phosphate buffer (pH 7).

The development of biocathode has also been investigated. To facilitate electron transfer between the electrode surface and the redox protein centers, the concept of co-deposition of MCNTs within the bio-electrocatalytic film has also been pursued here. To stabilize composite films, we utilize MCNTs modified with ultra-thin layers of organic (e.g. 4-(pyrrole-1-yl) benzoic acid[1]. We expect here attractive electrostatic interactions between anionic adsorbates and positively charged domains of the enzymatic sites. Other important issues are stability and mediating capabilities of adsorbates. We have also utilized metalloporphyrin redox centers (at which the reduction of oxygen, mostly to hydrogen peroxide, is initiated) and such an enzyme as horseradish peroxidase (HRP), or cabbage peroxidase (CP), that is capable of catalyzing electroreduction of hydrogen peroxide to water as a final product. Co-existence of the above components leads to synergistic effect that is evident from some positive shift of the oxygen reduction voltammetric potentials (more than 50 mV in citrate buffer) and significant increase of voltammetric currents (relative to those of the enzyme-free system). The film has also exhibited relatively higher activity towards reduction of hydrogen peroxide. It is reasonable to expect that the reduction of oxygen is initiated at cobalt porphyrin redox centers, and the undesirable hydrogen peroxide intermediate is further reduced at the horseradish or cabbage peroxidase enzymatic sites.

REFERENCE

1. Kowalewska B., Skunik M., Karnicka K., Miecznikowski K., Chojak M., Ginalska G., Belcarz A., Kulesza P. J.: Electrochim. Acta *53*, 2408 (2008).

## OP32
## KINETICS OF CORROSION AND DISSOLUTION OF URANIUM DIOXIDE IN AQUEOUS SOLUTIONS

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Within the framework of the geological disposal of spent nuclear fuel, research on the long term behaviour of spent fuel is undertaken and in particular the study of mechanisms of $UO_2$ oxidation and dissolution in water-saturated host rock. In this context, the redox behaviour of uranium on a rotating $UO_2$ disk electrode in conditions leading to the uranyl ion formation was investigated.

The first part of this work is to optimize faradic yields of electrochemical oxidation of uranium (IV) to uranium (VI) and to determine the exchange current density, $j_0$, the anodic charge transfer coefficient, $\alpha$, and the corrosion potential, $E_{corr}$, using the Butler-Volmer equation which is applicable when the reaction rate is controlled by the charge-transfer process. An experimental design[1] is used to optimize values of the significant experimental variables: the scan rate (v) and the rotation rate (w). The other chemical parameters of reactional media (pH and uranium concentration) are kept as nearly constant as possible.

The second part of this work is to study the influence of pH and carbonate ions[2] on the $UO_2$ dissolution kinetics. This study will afford a validation of the coupling of the developed electrochemical model to thermodynamics aqueous speciation.

Completing the electrochemical study, the characterisation of the solid by XPS, SEM and XRD is performed directly on the sample after voltametry measurements.

*The authors are grateful to Electricité de France (EDF) and ANDRA for their financial support within the Research Program on the long term Evolution of Spent Fuel of the CEA (PRECCI).*

REFERENCES

1. Doehlert D. H.: Appl. Statistics *19*, 231 (1970).
2. Shoesmith D. W.: J. Nuc. Mat. *282*, 1 (2000).

## OP33
## AN INNOVATIVE MICRO-ANALYTICAL FLOW SYSTEM BASED ON ELECTROCHEMICAL DETECTION FOR THE DEVELOPMENT OF RAPID AFFINITY TESTS

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In this work, the characterisation of a rapid and sensitive flow device based on electrochemical detection for affinity assays development is reported. This innovative system combines a special cartridge containing eight polymer microchannels, with a computer-controlled instrument for the control of fluidics. The advantage in using this platform is related to the higher surface-to-volume ratio obtained in the channels; actually, the walls of channels can be used as solid-phase for affinity reactions; then, the application of a suitable flow procedure to introduce the reagents can leads to shorter diffusion distances with very short reaction times. Finally, the presence of micro-electrodes in each channel allows the direct quantification of the affinity reaction by conducting eight in -parallel electrochemical measurements.

As first assay model, an indirect competitive assay format was carried out. The microchannels were used as solid-phase for rIgG immobilisation; then, a competition between an unknown amount of free rIgG and a fixed concentration of anti-rIgGalkaline phosphatase labelled was created directly in the modified channels. Finally, the substrate solution (paminophenyl phosphate 10 mM) was introduced and a real time amperometric evaluation of the enzyme kinetic was performed. Because all the steps of the immunoassay occurred through hydrodynamic loading of the different solutions through the channels, the speed (μl min$^{-1}$) and duration of the flow and incubation parameters were optimised. The effectiveness of the system was demonstrated by analysing rIgG concentrations in sample solutions within 5 min, obtaining the same sensitivities as well as in the ELISA tests. The system was also used as platform for affinity experiments using DNA coupled with paramagnetic particles. In this format both hybridisation and labelling events were performed on streptavidin-coated paramagnetic microparticles functionalised with a biotinylated capture probe. After sandwich hybridisation with the complementary sequence and a biotinylated signalling probe, the hybrid was labelled with a streptavin-alkaline phosphatase conjugate. The particles finally modified were then introduced in the channels of the cartridge, in which were trapped with a special magnet before to introduce the substrate and to carry out the electrochemical measurement. The advantage of this approach is that channels can be regenerated after each assay; particles can be released by removing the magnet and after washing the cartridge can be re-used for a new assay.

This protocol was applied to the analytical detection of PCR amplified samples; obtained results demonstrated that the analytical procedure based on the use of paramagnetic beads allowed the possibility to measure nM level of DNA sequences, with high reproducibility.

## OP34

## TAILORING SURFACES AND SUPPORTS FOR ENZYME MEDIATION, WITH APPLICATION TO BIOSENSOR AND BIOPOWER DEVICE DEVELOPMENT

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In this presentation we report on the synthesis and the characterization of redox complexes that possesses properties suitable for both redox catalysis (mediation) and immobilization chemistry at pre-functionalized surfaces and supports. The complexes can be attached to supports previously grafted to pre-functionalized surfaces to yield stable three dimensional redox layers. Subsequent co-immobilization of biocomponents in these layers provides a toolbox for rational development of prototype electrochemical biosensors and biocatalytic fuel cell systems (Fig. 1).

Tailoring of surfaces by pre-functionalization can be achieved through formation of alkanethiol layers on gold or, more recently, the use of aryl diazonium salts for chemical functionalization of a variety of surfaces. This provides a suitable platform for chemical grafting of a library of mediating redox complexes and polymers, developed in Galway, to yield redox-active layers of improved stability on electrode surfaces. The components in the mediator library can then be co-immobilized with redox enzymes to investigate optimal combinations of mediator and enzyme to provide biosensor or biopower devices. Further improvements in device performance can be gained by engineering the surface to yield increased macro- and microscopic surface roughness of the underlying electrode.

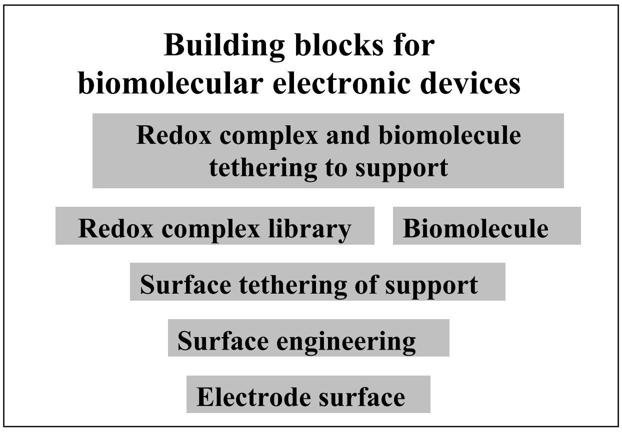

Fig. 1. **Schematic depiction of the toolbox available for rational design and optimization of electrode surfaces and supports to provide bioelectrochemical devices**

## OP35

## SILICATE CONFINED IONIC LIQUID FOR ELECTRODE MODIFICATION

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In last few years a number of studies reporting electrochemical behaviour of ionic liquid deposit on different electrode supports appeared in literaure[1–4]. These systems were used to study various electrochemical processes including ion transfer across the ionic liquid/aqueous solution interface.

We applied the method based on the sol-gel process where the cations from the ionic liquid act as sol-gel precursor[5,6] for electrode modification[7]. A thin silicate film containing imidazolium cationic groups surface was obtained by sol-gel processing of ionic liquid – 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium bis(trifluoromethyl-sulfonyl)imide (***I***) together with tetramethyl orthosilicate (***II***) on the indium tin oxide electrode. The formation of silicate film was confirmed by FTIR spectroscopy. This electrode act as a sponge for electroactive ions present in aqueous solution. The accumulation is much more effective than for electrode covered by ionic liquid precursor. The repelling of $Ru(NH_3)_6^{3+}$ cations by this electrode is also demonstrated.

The same approach was used for synthesis of silicate mesoporous submicrometer particles modified with covalently bonded ionic liquid *via* Stober method[8] coupled with surfactant templated[9] hydrolysis – co condensation of ***I*** and ***II***. The carbon paste electrode was prepared by mixing together carbon particles, new hybrid material particles and hexadecane as a binder. Electrochemical properties of this electrode were investigated with cyclic voltammetry and significant anion accumulation effect has been also found.

REFERENCES

1. Wadhawan J. D., Schroder U., Neudeck A., Wilkins S. J., Compton R. G.. Marken F., Consorti C. S., de Souza R. F., Dupont J.: J. Electroanal. Chem. *493*, 75 (2000).
2. Tanaka K., Nishi N., Kakiuchi T.: Anal. Sci. *20*, 1553 (2004).
3. Niedziolka J., Rozniecka E., Stafiej J., Sirieix-Plenet J., Gaillon L., Di Caprio D., Opallo M.: Chem. Commun. *2005*, 2954.
4. Rozniecka E., Niedziolka J., Murphy M. A., Sirieix-Plenet J., Gaillon L., Marken F., Opallo M.: J. Electroanal. Chem. *587*, 133 (2006).
5. Mehnert C. P., Cook R. A., Dispenziere N. C., Afeworki M.: J. Am. Chem. Soc. *124*, 12932 (2002).
6. Valkenberg M. H., deCastro C., Hölderich W. F.: Green Chem. *4*, 88 (2002).
7. Lesniewski A., Niedziolka J., Palys B., Rizzi C., Gaillon L., Opallo M.: Electrochem. Commun. *9*, 2580 (2007).
8. Stober W., Fink A., Bohn E.: J. Colloid. Interface Sci. *26*, 62 (1968).
9. Monnier A. : Science *261*, 1299 (1993).

## OP36

## MANGANESE DETECTION IN RIVER WATER BY ANODIC STRIPPING VOLTAMETRY USING ROTATING Hg-Ag AMALGAM ELECTRODE

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In aquatic systems, dissolved metals, even present at trace levels are generally accumulated all along the trophic chain and may result in a global contamination of the biota. For instance, manganese, an essential micronutrient for all organisms, can be very toxic at high concentrations and contribute for example to the development of Parkinson's symptoms. Generally detected at very low concentration level in the oxygenated freshwater, its concentrations can also increase temporarily but drastically when sediment porewaters are mixed with the overlaying water during intensive fluvial traffic.

At the present time, various techniques for the manganese analysis are used, mostly atomic emission and absorption spectrometry. However, these techniques necessitate sampling, pre-treatment (including filtration and acidification) and analyses in the laboratory.

The purpose of this work consists in the development of a new voltametric method for the determination on-line and on-site of electrolabile manganese in river, using a rotating Hg-Ag amalgam electrode. For a deposition time of 1000 s, a detection limit of 5 ppb for manganese in freshwater has been obtained by differential pulse anodic stripping voltametry. Well-defined peaks of manganese between 30 to 1000 ppb have also been observed without addition of any reagents for 500 s deposition time. Moreover, several potentially important metallic interactions (like Pb, Zn or Ni) with manganese have been tested in this study. Finally, a preliminary environmental application has been carried out in the Deûle River after sediment remobilisation during the passage of a barge.

REFERENCE

1. Mikkelsen Ø., Schrøder K. H.: Electroanalysis *16*, 386 (2004).

## OP37

## THE USE OF IMPEDANCE SPECTROSCOPY FOR THE DETECTION OF DNA AND ANTIBODIES BASED ON RESTRICTED CHARGE TRANSFER

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Impedance spectroscopy is a versatile method for monitoring interfacial and bulk properties of the material under investigation. In recent years the method has also found application as transduction principle for analytical purpose. Binding reactions on electrode surfaces are particularly suited for a quantitative detection[1].

The interfacial impedance of a redox conversion such as ferri-/ferrocyanide is particularly sensitive to the accumulation of charge at the interface. Because hybridisation alters the charge situation the impedance technique can be applied for the discrimination of ss-DNA and ds-DNA.

For a gold chip electrode and immobilised ss-DNA (ref.[2]) only a small increase was found for the interfacial capacitance after ds formation (~5 %), however the charge transfer resistance $R_{ct}$ increased by a factor of about three for an 18-mer oligonucleotide. The relative change of $R_{ct}$ can be used for a sensorial DNA detection. There is a considerable influence of the ionic strength on the measurement. Sensitivity for oligonucleotides in the nanomolar concentration range can be achieved. Length of the DNA was varied here from a 18mer to a 37mer. Binding of organic dyes of different charge underline the idea that the changed charge situation at the sensor surface govern the impedimetric response upon hybridisation.

Impedimetric analysis of modified gold electrodes can be also used for a sensitive measurement of antibodies in serum samples[3]. The formation of an antigen-antibody complex on the electrode restricts the access of ferri-/ferrocyanide and thus results in an impedance increase. The antigen-antibody interaction can be directly monitored, however an amplification step is necessary in order to provide reproducible results and sensitivity for μmolar concentrations. It can be also shown that a sensitive analysis is achieved with screen-printed electrodes which allow a disposable sensor use. Furthermore a strategy for simplification of the impedance measurement can be introduced based on an equivalent circuit analysis. Applicability of the impedimetric sreen printed electrodes can be shown by a comparative serum analysis of autoantibody concentrations against tissue transglutaminase which are developed during coeliac disease.

REFERENCES
1. Lisdat F., Schäfer D.: Anal. Bioanal. Chem., in press.
2. Pänke O., Kirbs A., Lisdat F.: Biosens. Bioelectron. *22*, 2656 (2007).
3. Balkenhohl T., Lisdat F.: Anal. Chim. Acta *597*, 50 (2007).

### OP38

## ASSESMENT OF FREE RADICALS POTENTIAL TOXICITY USING LIPOPROTEIN BIO-MIMETIC SYSTEMS

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The complex processes occurring on the cell membranes suppose equilibriums developed in a multi-phase media, the path-evolution of the free radicals (FR) damaging action supporting various hypothesis, theoretical models and experimental data, but not all supplied a response noteworthy as physiological relevant information.

The main objective of present work was to develop a bio-mimetic sistem applicable to free radicals analysis, that provides by an electrochemical approach a biological significant response.

The design of the bio-mimetic system was based on human lipoproteins (low-density and very low-density lipoproteins) shell deposition on a metal nanoparticle (Au-Np-less than 100 nm diameter) core, resulting a bio-mimetic composite. Subsequently the bio-mimetic composite was deposed on a conductive solid support (cleaned without oxides traces Au sheets; functionalised ITO) in a biosensing structure. The procedure of bio-mimetic system development was optimised (AuNp amount, deposition time, temperature, lipoprotein amount). Free radicals – $HO^{\bullet}$ (thermal generated via 10 mmol $L^{-1}$AAPH) and superoxide- induce a structural modifications of the deposed lipoprotein shell, initiating lipoperoxidation ($LOO^{\cdot}$) which is the main damaging compound generated by FR excess. Those lipoprotein structural modifications rise an electrical measurable signal, the degree of peroxidation correlating with the sample free radical concentration and damaging effect. The information is quantified as difference on the signal registered in the absence of free radicals, denominated reference (normal status, used as blank signal) and that registered in the presence of free radicals, denominated indicator (biological hazardous status). The biomimetic developed system was calibrated on a FR concentration range of $10^{-9}$–$10^{-6}$ mol $L^{-1}$ to real samples (gases and physiological samples). The system was validated in terms of applicability, linearity, sensitivity (limit of detection) repeatability, and reproducibility. The structural FTIR confirmation of the FR damaging effect was performed. The efficacy of ubiquinone either as external preservative or embedded one was assessed on a concentration range of 4 to 420 ppm, the HPLC confirmation of the results being attempted.

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### OP39

## INTRAMOLECULAR ELECTRONIC INTERACTIONS IN TWO TYPES OF DICARBONYL COMPOUNDS AND THEIR DERIVATIVES – AN ELECTROCHEMICAL AND QUANTUM CHEMICAL STUDY

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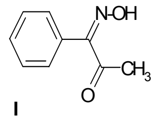
Molecules with two (or more) redox centers that are vicinal or connected by an unsaturated bridge, due to the intramolecular electronic interactions, exhibit often special redox properties that do not correspond to the sum of original characteristic properties of each of the centers. The most recent example has been observed in our investigation of reduction mechanisms of various oximes in buffered aqueous media[1]. A significant difference in electroreduction mechanism has been found for two isomeric oximes of aryl alkyl 1,2-diketones in acidic and neutral media[2].

The reduction of 1-phenyl-2-oxo-1-oximinopropane (***I***) in acidic media follows the expectable pathway common for most oximes (i.e. a four-electron reduction yielding the corresponding α-aminoketone which is further reduced to the benzyl methyl ketone). The isomeric 1-phenyl-1-oxo-2-oximinopropane (***II***), however, is reduced under polarographic or voltammetric conditions in a four-electron wave to the non-reducible 1-hydroxy-2-amino olefin (***III***), which is stable enough to be detected and proved and which is very slowly



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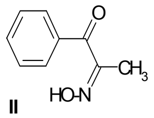

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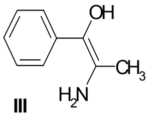

III

further converted to the tautomeric α-aminoketone.

The difference appears in the second two-electron step where the intermediate α-ketoimine (generated in the first two-electron reduction step of the parent oxime) is further reduced: In the case of (***I***) only imin is reduced to amin, in the case of (***II***) a two-electron reduction of 1,2-diprotonated iminoketon leads to the olefin (***III***).

The latter behavior is analogous to that of benzil[3] and in many aspects similar to the reduction of 1,4-diacetylbenzene[4]: both mentioned symmetric dicarbonyl compounds are reduced in acidic media in a single two-electron wave yielding an enediol and a quinonemethide, respectively, even when their molecules contain two reducible, conjugated carbonyl groups.

The common reason of the mentioned "symmetric" reductions is the symmetry of LUMO orbitals, which are able to accept two electrons “simultaneously”. The goal of this study is the finding, that the asymmetric molecule ***II*** (in contrast to ***I***) has a symmetric LUMO orbital and therefore follows the reaction pathway of benzil. The quantum chemical approach confirmed theoretically the above electrochemical experimental results, In addition to this, a crucial difference in the N-C-C-O dihedral angle of ***I*** and ***II*** was also proved.

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REFERENCES

1. Celik H., Ludvík J., Zuman P.: Electrochim. Acta *52*, 1990 (2007).
2. Celik H., Ludvík J., Zuman P.: Electrochem. Commun. *8*, 1749 (2006).
3. Vincenz-Chodkowska A., Grabowski Z. R.: Electrochim. Acta *9*, 789 (1964).
4. Kargin J., Manousek O., Zuman P.: J. Electroanal. Chem. *12*, 443 (1966).

## OP40

## MONITORING OF NON-IONIC SURFACTANTS IN THE AQUATIC ENVIRONMENT THROUGH THEIR ENTRAPMENT IN A PTFE CAPILLARY TRAP AND INDIRECT TENSAMMETRIC DETERMINATION

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Non-ionic surfactants (NS) are a major pollutant of the aquatic environment due to their common use in washing and cleaning. Unfortunately, NS are rarely monitored in the aquatic environment, mainly because of the high cost and time-consuming nature of the standard methods of determination. The indirect tensammetric technique (ITT), together with separation of NS through their entrapment in a PTFE capillary trap (PTFECT), provides an opportunity for fast and inexpensive monitoring of NS in the aquatic environment.

ITT is an electroanalytical technique which takes advantage of capacitance phenomena. A sinusoidal alternating current curve is recorded. In the presence of surfactants, adsorption-desorption peaks called tensammetric peaks appear on the curves. In ITT, the tensammetric peak of the monitoring substance (usually ethyl acetate) is recorded. The lowering of the monitor peak due to competitive adsorption of the investigated surfactants is the analytical signal in ITT. This approach is much better suited to surfactant analysis than the direct recording of surfactant peaks. The analytical response is only partly selective. This means that separation of NS from the water matrix is necessary prior to the determination. This can be done by liquid-liquid extraction or solid phase extraction; however the simplest approach is to use PTFECT.

In order to demonstrate the applicability of ITT with PTFECT for NS monitoring in the aquatic environment, NS were monitored in several places along the River Warta and its small tributaries Gluszynka and Cybina (all near Poznan, Poland) over a period of one year. These two tributaries flow through series of lakes. The results show the cleaning effect of Lake Malta in terms of NS reduction.

## OP41

## SURFACE, ELECTROCHEMICAL AND ELECTROANALYTICAL PROPERTIES OF POLYMER MODIFIED ELECTRODES

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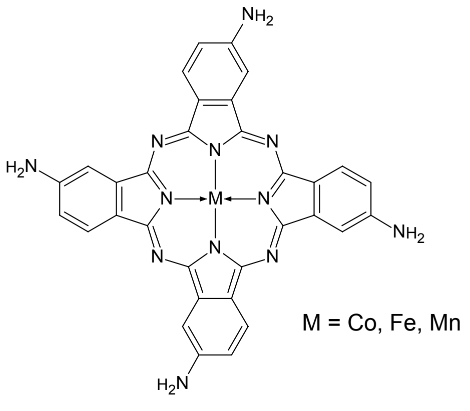
The quest to find new and stable materials that can be used to modify electrodes is of interest. This is due to the fact that the modified electrode systems have been found to yield very important analytical devices for various electrochemical



Scheme 1. **Molecular structure of the polymerizable tetra amino metallo phthalocyanine (TAMPc) complexes**

sensor applications. The bare or conventional electrodes operate at unfavourably high anodic or cathodic potentials. The investigation into materials that (*i*) are stable, (*ii*) can be used as electrode modifiers and (*iii*) can lower the working potentials are desirable. Redox polymers have been widely investigated as potential electrode modifiers for the fabrication of electrochemical sensors and biosensors. The electrocatalytic activities of redox polymers are mediated by their redox active sites. This work investigates the use of polymers of tetraamino metallo-phthalocyanine (TAMPc) complexes which are highly stable (as electrode modifiers) in various conditions and have remarkable catalytic activities. Surface and electrochemical properties of polymerizable TAMPc complexes on various electrode surfaces and their electrocatalytic activities towards the detection and quantification of $H_2O_2$ will be presented.

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## OP42

## RESPONSE BEHAVIOUR OF AMPEROMETRIC GLUCOSE BIOSENSORS BASED ON DIFFERENT CARBON SUBSTRATE TRANSDUCERS COATED WITH ENZYME-ACTIVE POLYMER LAYER: A COMPARATIVE STUDY

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Since the number of patients with diabetes is rapidly increasing worldwide, the designing and preparation of selective, stable, reliable and low cost glucose sensors continues to be an extremely interesting field of investigation. Classical electrochemical glucose biosensors involve glucose oxidase, which allows determining glucose via hydrogen peroxide, produced during the enzyme reaction. One of the problems in this approach is a high overpotential needed for hydrogen peroxide oxidation or reduction and, therefore, the application of an appropriate catalytic mediator is considered as a significant improvement[1]. However, there are several important factors, such as substrate transducer size and shape, enzyme immobilization strategy, etc., that are still open in tailoring the biosensor response to a desired behaviour.

In this contribution we present a comparative study with respect to the response characteristics and the overall performance of amperometric glucose biosensors based on different carbon substrate transducers coated with glucose oxidase (GOx) entrapped polymer membrane and the iron-ruthenium hexacyanoferrate (FeRuHCF) as a hydrogen peroxide detection mediator. Using potentiodynamic deposition protocol, FeRuHCF was first grown onto the surface of either a carbon fibre, screen-printed carbon or glassy carbon substrate electrodes of different sizes and geometries while GOx was subsequently immobilized into a potentiostatically coated polymer membrane. Effect of various biosensor preparation (including polymerization) parameters, such as polymerization time and GOx concentration, were carefully examined. Under the hydrodynamic amperometric conditions at an operating potential of –0.02 V *vs.* Ag/AgCl, the current response characteristics (linearity, range, sensitivity, response time, etc.) of the investigated biosensors for measuring glucose at the physiological pH were systematically studied and compared.

REFERENCE

1. Pauliukaite R., Hocevar S. B., Hutton E. A., Ogorevc B.: Electroanalysis *20*, 47 (2008).

## OP43

## DETECTION OF INFLUENZA VIRUS A BY USING IMPEDIMETRIC BIOSENSOR

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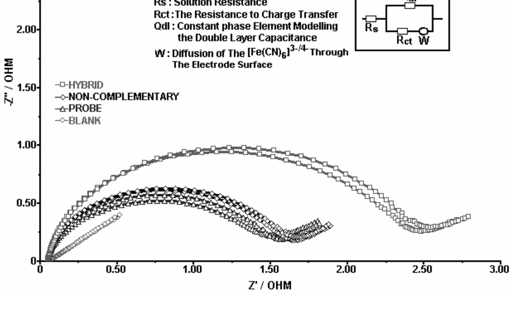
In this study, label free DNA probe sequences related to the influenza type A virus and its complementary target sequences were detected by monitoring the changes in surface impedance of the pencil graphite electrode (PGE), before and after hybridization process. The analysis of the hybridization behaviour was realised in the presence of $[Fe(CN)_6]^{3-/4-}$ (ref.[1,2]). After addition of the complementary oligonucleotide to the ssDNA (probe) modified PGE electrode, an increase of the electron transfer resistance ($R_{ct}$) was observed. The response of the probe modified PGE which was interacted with a non-complementary sequence resulted in same as probe modified PGE surface impedance and proved the specifity of the hybridization with target[3,4]. System was applied to the synthetic oligonucletides related to the virus DNA. Impedimetric biosensors are a class of electrochemical biosensors that show great promise for they have potential for simple, rapid, label-free and low-cost detection of biomolecules such as DNA. It is also possible to detect



different kind of target analytes by simply varying the probe used with Impedimetric biosensors.

Nyquist plots before and after hybridization with both complementary and non-complementary sequences.

REFERENCES

1. Steichen M., Buess-Herman C. : Electrochem. Commun. *7,* 416 (2005).
2. Steichen M., Decrem Y., Godfroid E., Buess-Herman C.: Biosens. Bioelectron. *22*, 2237 (2007).
3. Eskiocak U., Ozkan-Ariksoysal D., Ozsoz M., Oktem H. A. : Anal. Chem. *79*, 8807 (2007).
4. Ozkan-Arıksoysal D., Tezcanlı B., Kosova B., Ozsoz M.: Anal. Chem. *80*, 588 (2008).

## OP44

## PCR-COUPLED ELECTROCHEMICAL DETECTION OF *Legionella pneumophila*

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*Legionella pneumophila* is an important human pathogen responsible for Legionnaire's disease and an environmental pollutant worldwide. According to legislation, the standard method for analysis of *L. pneumophila* in water samples is based on cellular cultures which involve a long incubation period of time. Specific detection based on its genetic material could be also developed.

Conventional Polymerase Chain Reaction (PCR) is the most widely method for nucleic acid amplification but it provides only qualitative data. Alternatively, real-time PCR allows the quantitative detection of genomic sequences but due to the cost and sophistication of the instrumentation, it is generally limited to use in research laboratories.

Electrochemical genosensors represent an interesting approach because of their intrinsic characteristics such as real-time detection, fast analysis time, low cost and simplicity. A voltammetric genosensor for *L. pneumophila* has been previously described[1] which reported good analytical performance, including an enhanced selectivity. Briefly, a sandwich-hybridization format assay was combined with an immobilized stem-loop DNA structure as capture probe and a biotinylated sequence as signalling probe to detect a 52-mer specific sequence. The resulting biotinylated ternary hybrid was labelled with the enzymatic conjugate streptavidin-alkaline phosphatase and subsequently incubated with an electrochemically inactive substrate, 1-naphthyl phosphate. The amount of 1-naphthol enzymatically generated was determined by Differential Pulse Voltammetry (DPV).

To achieve the challenging sensitivity demanded by environmental legislation, we have developed a method based on coupling the voltammetric genosensor with conventional PCR, technique available in most of routine laboratories. Samples are amplified by PCR and analyzed by the genosensor. The obtained signal was compared with a calibration plot for a 95-mer synthetic target with the same length as the amplicon. PCR conditions (temperatures, cycle number and primers) were optimized to get the reliable detection of $10^2$ copies of *L. pneumophila* as well as to distinguish $10^3$ and $10^4$ copies of the pathogen, values also related to corrective actions in water systems buildings.

*R.M.C. thanks the Spanish MEC for a FPU grant.*

REFERENCE

1. Miranda-Castro R., de-los-Santos-Álvarez P., Lobo-Castañón M. J., Miranda-Ordieres A. J., Tuñón-Blanco P.: Anal. Chem. *79*, 4050 (2007).

## OP45

## VOLTAMMETRIC SIGNALS CALCULATED BY INFINITE SERIES APPROACH

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The objective of this work is to apply or develop effective transformation of infinite series providing analytical solution for calculation of current – potential curves in LSV and CV, in order to include the region of potentials, in which the original series are not converging. The developed methods enable accurate calculation of the I – E curves in the following cases: (a) common LSV & CV with reversible charge transfer[1,2], (b) common LSV with irreversible charge transfer[1], (c) LSV under finite diffusion space conditions[3], applicable in thin-layer electrochemistry and redox polymer films, (d) intercalation processes assuming different structural dimensionality (one-, two-, and three dimensional diffusion space)[4].

The form of current – potential curves, their peak height and position vary significantly with the thickness of the film of the host material. It is expressed by dimensionless parameter *L*, composed of the real film thickness, scan-rate and diffusion coefficient in the solid phase. For large *L* values the calculated current – potential curves have the same form as typical for conventional linear scan voltammetry with reversible and irreversible electrode reaction, resp. For low *L* values, a thin-layer electrochemistry bahaviour is demonstrated as the second extreme.

The shape, magnitude, and position of voltammogram depend, besides dimensionless thickness *L*, also on the heterogeneous rate-constant and transfer coefficient (for irreversible reaction), dimensionality factor describing the way of diffusion in the host lattice, and also on the ratio of the diffusion coefficients of the intercalated ions and their concentration in the solid and liquid phase, respectively. Calculated dependences of peak current and peak potential on parameter *L* make possible to discover how the way of diffusion (one-, two-, or three- dimensional) affects the shape of voltammogram. From the peak current vs. scan-rate dependence it is also possible to calculate real values of the solid-phase diffusion coefficients of intercalated ions, which in general are considerably smaler compared to their values in the solution.

*The help of Prof. Alan Bond of Monash University, Clayton, Victoria as well as the support of this work by grant APVV-0057-06 are highly acknowledged.*

REFERENCES

1. Mocak J.: Electrochem. Commun. *4*, 803 (2002).
2. Mocak J., Bond A.: J. Electroanal. Chem. *561*, 191 (2004).
3. Aoki K., Tokuda K., Matsuda H: J. Electroanal. Chem. *146*, 417 (1983); *160*, 33 (1984).
4. Armand M., Dalard F., Deroo D., Mouliom C.: Solid State Ionics *13*, 205 (1985).

## OP46

## REDOX ACTIVE LAYERED DOUBLE HYDROXIDES FOR GLUCOSE BIOSENSOR DEVELOPMENT

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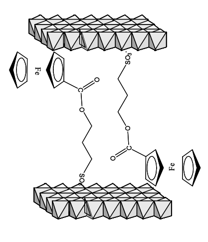
Layered double hydroxides (LDH) are a family of synthetic lamellar materials with interlayer space containing anions. Organic electroactive anions such, 2,2'-azinobis 3-ethyl--benzothiazoline-6-sulfonate (ABTS) and anthraquinone sulfonate have been intercalated within LDH interlayer domain, giving well characterized nanohybrid materials[1]. We have successfully fabricated electrochemical biosensors based on the immobilization of horseradish peroxidase, laccase and nitrite reductase within these redox active LDH; the intercalated redox mediators playing the role of electron shuttle between the enzymes and the electrode[2–4].

A new LDH nanohybrid containing a ferrocene derivative (FcPS) was synthesized by the coprecipitation method and characterized by XRD, FTIR and electrochemistry (Scheme). The resulting hybrid material was used for the immobilization of Gox. The present biosensor configuration differs from that described by Dan Shan, where ferrocene methanol was simply adsorbed on the LDH particles. Analytical characteristics of different glucose biosensors based on LDH matrices will be examined in relation to their different configurations.

| LDH | Redox medatior | Ref |
|---|---|---|
| ZnAl-Cl | – | 5,6 |
| $NiAl-NO_3$ | – | 7 |
| ZnCr-ABTS | ABTS | 2 |
| ZnAl-Cl | FcMOH | 8 |
| ZnCr-FcPS | FcPS | – |

Configurations of Gox biosensors



Scheme of ZnCr-FcPS

REFERENCES

1. Therias S., Mousty C., Bonnet S., Forano C., Palvadeau P.: Mol. Cryst. Liq. Cryst. *311*, 195 (1998).
2. Shan D., Cosnier S., Mousty C.: Anal. Lett. *36*, 909 (2003).
3. Mousty C., Vieille L., Cosnier S.: Biosens. Bioelect. *22*, 1733 (2007).
4. Chen H., Mousty C., Cosnier S., Silveira C., Moura J. J. G., Almeida M. G.: Electrochem. Comm. *9*, 2240 (2007).
5. Cosnier S., Mousty C., Gondran, Lepellec A.: Mat. Sci. Eng., C *26*, 442 (2006).
6. Shan D., Yao W., Xue H.: Electroanalysis *18*, 1485 (2006).
7. Mignani A., Luciano G., Lanteri S., Leardi R., Scavetta E., Tonelli D.: Anal. Chim. Acta *599*, 36 (2007).
8. Shan D., Yao W., Xue H.: Biosens. Bioelect. *23*, 648 (2007).

## OP47

## OH-CHIP IMPEDIMETRIC DETECTION OF VIABLE PATHOGEN BACTERIA

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The determination of some important pathogen bacteria in solution has been attempted using electrochemical impedance spectroscopy (EIS) on chip. Bacterial presence in solution can not change electrical properties of the medium. However, their ability to adhere on almost any surface can be employed to monitor them. On the other hand, a high adhesion reduces the capacity of the electrodes to evaluate the electrical change produced. Bipolar impedance measurements, employing in-house built chip electrodes, were performed to check the electrical change produced by different gram negative bacteria (Escherichia coli, Salmonella and Pseudomonas aeruginosa) in solutions of constant conductivity. The data recorded in a high range of frequencies showed the influence of bacterial presence in the interface properties in opposition of the solution properties which remained almost constants. Bacterial concentration was shown to be easily monitored by using electrochemical impedance spectroscopy (EIS) throughout the change produced in the electrode-electrolyte interface. In fact, bacteria were monitored through the double layer capacitance value obtained at low frequency. Several transducer materials and configurations were employed as working microelectrodes (Pt, C and ITO). Although each material showed a different capacity to response to the changes produced by bacteria, electrode configuration was shown to be the most limiting parameter.

Bacteria are small prokaryotic and unicellular microorganisms with a huge variety resources adapt to any metabolic restriction and environmental condition. Thus, bacterial species can be found adapted to live anywhere (air, water or soil), even in very restrictive environments, as free cells (planktonic cells) or in communities, such as biofilms[1]. The determination of the concentration of planktonic bacteria in liquids is important in different fields[2]. Thus, the monitoring of the concentration of suspended bacteria is especially relevant in the fermentation industries where a strict control of the concentration of cells in the incubator is absolutely necessary during the fermentation process.

On the other hand, the presence of bacteria, even the non-pathogenic ones, is very restricted in other areas, namely the environmental monitoring, the food and the beverage industries and the clinical chemistry. For instance, the presence of non-pathogenic bacteria in drinking water is limited to $10^2$ colony forming units per ml (CFU $m\,l^{-1}$)[3]. Thus, these areas require fast and simple to continuously quantify planktonic bacteria in liquids, especially at low concentrations.

Conventional methods for the detection of viable bacteria typically rely on the culture-based assays. Among all well-known measurements techniques, but from an electrochemical viewpoint, impedance spectroscopy has become widely used for the study of biological systems – from lipid membrane to medical imaging[4].

This work describes a simple and fast impedimetric approach on chip for the monitoring of the concentration of suspended pathogen bacteria (gram negative) based on the changes produced in the electrode-solution interface by the early bacteria attachment on different type of microelectrodes. The effect of the size of the counter electrode, the influence of the applied potential, the transducing material and the aging of the sensor are also investigated.

Impedance spectroscopy was found to be particularly sensitive to the very early attachment/pre-attachment. The magnitude of the interface capacitance could be correlated with the concentration of suspended bacteria. The sensitivity of the interface capacitance could be enhanced by applying more positive potentials on the working electrode which favoured bacterial attachment. In terms of aging, sensors lost the capacity to discriminate between concentrations with time, especially at low concentrations.

As a more emphasized result, for platinum microelectrodes, the double layer capacitance magnitude increases with the concentration of suspended Pseudomonas (rather than decreases as seen at longer times) with an evident correlation from $10^1$ to $10^7$ CFU $m\,l^{-1}$.

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REFERENCES

1. Madigan M. T., Martinko J. M., Parker J.: *Brock Biology of Microorganisms*, Prentice Hall International, Hertfordshire 1997.
2. Tang H., Zhang W., Geng P., Wang Q., Jin L., Wu Z., Lou M.: Anal. Chim. Acta *562*, 190 (2006).
3. Lebaron P., Henry A., Lepeuple A. S., Pena S., Servais P. : Marine Pollution Bulletin *50*, 652 (2005).
4. Ireland R. H., Tozer J. C., Barker A. T., Barber D. C.: Physiol. Measure *25*, 775 (2004).

## OP48
## SENSORS BASED ON SOLID COMPOSITES IN ELECTROCHEMISTRY OF BIOLOGICALLY ACTIVE COMPOUNDS

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Utilization of traditional mercury electrodes limits wider application of voltammetry in common laboratory practice. The cause of it consists in fears of toxicity of liquid mercury in last decades (however, from the toxicological point of view, the liquid mercury is practically non toxic!). Therefore, the effort has been concentrated on development of non-toxic electrode material friendly toward the environment and thus compatible with so-called "green analytical chemistry". This contribution describes recent results regarding voltammetric determination of submicromolar concentrations of various environmentally important biologically active substances using non-traditional types of electrodes: solid composite electrodes (SCEs)[1]. They belong to the group of composite electrodes with randomly distributed two or more components, which exhibit solid consistency. They are composed of at least one conductor phase (Au, Ag, amalgam etc.) mixed with at least one insulator phase (e.g., polyacrylate)[2]. Some other components can be added into bulk of the electrode or upon its surface material to achieve desired properties. Applications of CSEs are wide-spread: They have been applied for determination of heavy metals (Pb, Cd, Tl, Bi, As, etc.)[3–5], nitrates, nitrites[3], halides[6] as well as of many organic compounds (e.g., amino naphthalene, nitro naphthalene[7], nucleic bases[8], nitroquinoline, nitrobenziimidazole, metallothionein (Cd,Zn)[9], alizarine chrome black PT, phenylglyoxylic acid[10]).

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REFERENCES

1. Barek J., Fischer J., Navratil T., Peckova K., Yosypchuk B., Zima J.: Electroanalysis *19*, 2003 (2007).
2. Tallman D. E., Petersen S. L.: Electroanal. *2*, 499 (1990).
3. Navratil T., Kopanica M.: Crit. Rev. Anal. Chem. *32*, 153 (2002).
4. Navratil T., Kopanica M.: Chem. Listy *96*, 111 (2002).
5. Navratil T., Kopanica M., Krista J.: Chem. Anal.-Warsaw *48*, 265 (2003).
6. Sebkova S., Navratil T., Kopanica M.: Anal. Lett. *37*, 603 (2004).
7. Sebkova S., Navratil T., Kopanica M.: Anal. Lett. *36*, 2767 (2003).
8. Sebkova S., Navratil T., Kopanica M.: Anal. Lett. *38*, 1747 (2005).
9. Sestakova I., Navratil T.: Bioinorg. Chem. Appl. *3*, 43 (2005).
10. Navratil T., Senholdova Z., Shanmugam K., Barek J.: Electroanal. *18*, 201 (2006).

## OP49

## ELECTROCHEMICAL POTENTIAL IN QSPR/QSAR

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At the present time the methods of quantitative structure-property / structure-activity relationships (QSPR/QSAR) are increasingly developed in various areas of chemistry, biology, and pharmacy[1].

Although various physico-chemical properties are applicable for QSPR/QSAR studies, the oxidation-reduction properties (*e.g.,* half-wave potential) seem to be most advantageous, as they are supposed to be important in interactions of substance with biological systems and could be correlated with biological properties[2]. The relationships between electrochemical and biological properties carry a great significance, allowing the use of electrochemical parameters as direct evaluators of a biological activity. Electrochemical parameters do not give absolute correlation with biological activity data due to the enormous complexity of the live organism, so many other important factors (*e.g.,* membrane permeability) must also be considered.

Mention will be made of examples where electrochemistry contributes significantly to pharmacy or medical chemistry. Besides the classical Zuman work[3], the studies of acridines[4] or benzoxazines[5,6] could be noted as the examples of QSPR studies. There are only few QSAR studies using electrochemical potential for description of the effect of substituent on biological properties, such as inactivation of cytochrome P-450 (cit.[7]), antitumor activity[8], and antioxidant activity[9].

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REFERENCES

1. Hansch C., Leo A.: *Exploring QSAR. Fundamentals and Applications in Chemistry and Biology.* American Chemical Society, Washington 1995.
2. de Abreu F. C., de L. Ferraz P. A., Goulart M. O. F.: J. Braz. Chem. Soc. *13*, 19 (2002).
3. Zuman P.: *Substituent Effects in Organic Polarography*. Plenum Press, New York 1967.
4. Němcová I., Nesměrák K., Jelínek I., Němec I., Barbe J.: Anal. Lett. *34*, 1223 (2001).
5. Nesměrák K., Němec I., Štícha M., Waisser K., Palát K.: Electrochim. Acta *50*, 1431 (2005).
6. Toropov A., Nesměrák K., Raška I., Waisser K., Palát K.: Comput. Biol. Chem. *30*, 434 (2006).
7. Guengerich F. P., Willard R. J., Shea J. P., Richards L. E., Macdonald T. L.: J. Am. Chem. Soc. *106*, 6446 (1984).
8. Kunz K. R., Iyengar B. S., Dorr R. T., Alberts D. S., Remers W. A.: J. Med. Chem. *34*, 2281 (1991).
9. Yang B., Kotani A., Arai K., Kusu F.: Chem. Pharm. Bull. *49*, 747 (2001).

## OP50

## ELECTROANALYTICAL ASPECTS OF INTERACTIONS OF DsDNA WITH ANTICANCER INTERCALATING DRUGS

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Several voltammetric techniques used with graphite electrodes allow recording of reproducible anodic signals of dsDNA guanine. Some conditions, however, must be met to obtain readable signals: rigorous chemical and biological purity in the cell and appropriate purity of DNA are the must[1,2]. In this report we present an electroanalytical comparison of two anticancer drugs: C-1311 and C-1305 (both are derivatives of imidazoacridinone). Both: the agent and dsDNA are dissolved in the phosphate buffer solution. Pulse voltammetry and spectroelectrochemistry were employed in the investigation. Voltammetry allowed us to distinguish between the covalent- (intercalation of the drug), electrostatic- and groove-binding interactions and to obtain the corresponding binding constants.

Significant changes between both drugs were found. They included different number of the active sites occupied by one drug molecule and different nature of the weaker (other than the intercalation) interactions. In some experiments dsDNA was placed in a poly-(*N*-isopropylacrylamide) (NIPA) thermoresponsive gels to isolate the product of the intercalation process. Particularly interesting was the finding that the denaturation process of dsDNA is substantially slowed down after intercalation. This may be useful in designing new DNA sensors.

REFERENCES

1. Nowicka A., Zabost E., Donten M., Mazerska Z., Stojek Z.: Bioelectrochemistry *71*, 126 (2006).
2. Nowicka A. M., Zabost E., Donten M., Mazerska Z., Stojek Z.: Anal. Bioanal. Chem. *389* 1931 (2007).

## OP51

## ON-CHIP ELECTRIC FIELD DRIVEN ELECTROCHEMICAL DETECTION

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As a result of the rapid development within the field of lab-on-a-chip systems, there is currently a growing interest in miniaturised electrochemical devices[1]. This can be explained by the fact that electrochemical devices can be readily miniaturised and that the required electrodes can be manufactured with standard microfabrication techniques.

The main on-chip application of electrochemistry so far involves electrochemical detection in capillary electrophoresis (CE), a technique that has been employed for a wide range of applications[1,2]. The main problems associated with the of electrochemical detection in (conventional as well as on-chip) CE are caused by interferences due to the presence of the CE electric field[3,4] and uncertainties in the positioning of the electrodes with respect to the capillary which may affect the reproducibility of the measurements[1,2]. To mimimise the interferences of the CE electric field on the detection, the end column approach[1,2] is generally used in conjunction with on-chip devices due to its straightforward implementation. In this approach, a detection microelectrode is positioned immediately outside the end of the separation channel where the electric field strength is low enough to enable detection. The end column approach thus requires reproducible positioning of the detection electrode at the end of the separation channel which can be ensured by fixing the positions of the electrodes with respect to the channel during the micro fabrication process. However, the separation electric field still affects the detection via a change in the detection potential.

As has been shown by Klett et al.[5] the influence of the separation electric field on electrochemical detection can, however, be eliminated by ensuring that the detection and reference electrodes are positioned on an equipotential surface at the point of detection. It has also been shown[6] that the separation electric field in fact can be used for the detection by meauring the current between two microband electrodes positioned at the end of a CE capillary in the end column detection mode. In the latter case, a potentiostat was not required as the potential needed for the detection resulted from the potential difference induced between the electrodes as a result of the separation electric field and a small interelectrode distance. The latter technique should consequently be well-suited for use in conjunction with microfabricated flow channels in the presence of an external electric field.

This presentation will focus on our recent research[7] aiming at the development of electric field driven electrochemical detection techniques for inclusion in chip-based devices. It will be demonstrated that an external electric field can indeed be used to drive amperometric detection anywhere within a microfabricated flow channel containing an array of gold microband electrodes. The influence of parameters such as the electric field strength, the interelectrode distance, electrode stability and the concentration of electroactive species in the flowing solution on the detection will be discussed.

REFERENCES

1. Nyholm L.: Analyst *599*, 130 (2005).
2. Xu J.-J., Wang A.-J., Chen H.-Y.: Trends Anal. Chem. *125*, 26 (2007).
3. Wang K., He F.Y., Liu A. L., Xu J. J., Chen H. Y., Xia X. H.: Langmuir *7052*, 22 (2006).
4. Matysik F. -M.: J. Chromatogr., A *229*, 742 (1996).
5. Klett O., Björefors F., Nyholm L.: Anal. Chem. *1909*, 73 (2001).
6. Klett O., Nyholm L.: Anal. Chem. *1245*, 75 (2003).
7. Ordeig O., Godino N., del Campo J., Munoz F. X., Nikolajeff F., Nyholm L.: submitted to Anal. Chem.

## OP52
## AMPEROMETRIC IMMUNOSENSOR BASED ON POLYTHIONINE/GOLD NANOPARTICLES FOR THE DETERMINATION OF AFLATOXIN $B_1$

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In this study, an immunosensor was developed by electrodepositing gold nanoparticles on to a polythionine modified glassy carbon electrode (GCE).Anti-aflatoxin$B_1$ anti-body was immobilised on the modified GCE. Horseradish peroxidase was used to block sites against non-specific binding. Competition reaction was allowed to take place between the free $AFB_1$ and $AFB_1$-conjugate for the binding sites of the antibody. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were employed to characterize the electrochemical properties of the modified process. The current response decreased with an increase in AFB1 concentration in the range of 0–1.5 ng ml$^{-1}$ with a limit of detection of 0.4 ng ml$^{-1}$ at three times background noise. The proposed method eliminates the use enzymatic labels.

## OP53
## ENHANCING THE ELECTROCHEMICAL BEHAVIOR OF HEMOPROTEINS WITH CARBON NANOTUBE ELECTRODES

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Carbon nanotubes CNTs are attractive electrode materials due to their good electrical conductivity and mechanical strength, as well as their inertness in solution, where they still retain a high surface activity and a wide operational potential window. However, the proper construction and orientation of the carbon nanotube electrode is critical for its electrochemical properties; high density of open ends (similar to a graphite edge-planar electrode) can give fast electron transfer response but they only constitute a very small portion of the CNT surface exposed to the solution. Side-walls and amorphous carbon-covered surface dominate on the overall surface area, lowering the electron transfer kinetics. Moreover and from the point of view of the amperometric biosensing, the establishment of a fast electron transfer between the active site of a redox biomolecule and the electrochemical transducer is a desired feature to improve sensitivity.

Accordingly, our purpose is to highlight the transducer and biosensor performance of different electrode systems and configurations based on protein-modified carbon nanotubes and compare with graphite composites and highly oriented pyrolytic graphite. Amide bonds were formed to immobilize proteins, previous carboxylic activation of the carbonaceous element. Specifically, biosensing behavior of different configurations of carbon functionalized with redox proteins (myoglobin and catalase) will be evaluated. Such proteins exhibit high sensitivity to oxygen and peroxide, respectively, and catalyze their reduction, which can derive to oxygen and peroxide sensors. Our results confirmed that carbon nanotube electrodes constitute optimal environments for the direct electron transfer of such redox proteins. Additionally, we found that electrodes based on vertically aligned carbon nanotubes (nanotube forests) provide the highest electron transfer kinetics to the oxygen or peroxide reduction, the fastest sensor response and the highest signal/noise ratio, permitting the detection of very low analyte concentrations.

## OP54

## FIFTY YEARS OF NUCLEIC ACID ELECTROCHEMISTRY

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At present electrochemistry of nucleic acids is a booming field, particularly because of its actual and potential applications in biotechnologies. For example, it offers a simpler and less expensive alternative to optical detection in the DNA chips for parallel analysis of the DNA hybridization, DNA damage, DNA- and RNA-protein interactions, etc. First electrochemical nucleic acid experiments were done about 50 years ago with the dropping mercury electrode. In 1958* I showed that all nucleic acid bases, as well as DNA and RNA, are electroactive[1] producing cathodic and/or anodic signals on a.c. oscillopolarographic curves** (a.c. chronopotentiometry according to the present nomenclature). My results contrasted with the previously claimed electroinactivity of DNA and nucleic acid bases (except of adenine reduction in strongly acidic solutions)[2,3]. I identified the DNA cathodic and anodic signals[4] and showed that chromosomal native double-stranded (ds) DNA is not reducible in difference to reducibility of DNA degradation products. Shortly afterwards I showed that electrochemistry can be used to study DNA denaturation, renaturation and premelting[5]. We found (using different electrochemical methods) that electrochemical signals of dsDNA depend on its nucleotide sequence providing thus very early evidence of polymorphy of the DNA double-helical structure (reviewed in ref.[6]). For several decades DNA electrochemistry was studied by a handful of people, including laboratories of G. C. Barker, H. Berg (Jena), B. Czochralska (Warsaw), I.R. Miller (Rehovoth), H. W. Nürnberg (Jülich), J.A. Reynaud (Orleans) as well as V. Vetterl and V. Brabec in Brno, in addition to my laboratory. Their work laid down fundaments for the present flourishing field, including the development of DNA sensors. In 1978 solid electrodes were firstly used in nucleic acid research[7]. At the beginning of 1980's we introduced the first covalently bound electroactive marker into DNA[8] and several years later we proposed the first DNA-modified electrodes[9] (reviewed in ref.[10]). These findings paved the way for development of the DNA biosensors. Present state of DNA electrochemistry is reflected in recent reviews[10, 11], and particularly in the recently published book on the electrochemistry of nucleic acids and proteins[12]. In my talk the history of nucleic acid electrochemistry will be briefly summarized, and the present trends and perspectives in electrochemistry of nucleic acids and proteins in relation to biotechnologies and biomedicine will be discussed.

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REFERENCES

1. Palecek E.: Naturwiss. *45*, 186 (1958).
2. Bendich A., in: *The Nucleic Acids - Chemistry and Biology.* (Chargaff E., Davidson J. N., ed.), p. 119. Academic Press, New York 1955.
3. Berg H.: Biochem. Z. *329*, 274 (1957).
4. Palecek E.: Nature *188*, 656 (1960).
5. Palecek E., in: *Progress in Nucleic Acid Research and Molecular Biology*, (Davidson J. N., Cohn W. E., ed.), Vol. 9, p. 31. Academic Press, New York 1969.
6. Paleček E., in: *Progress in Nucleic Acid Research and Molecular Biology*, (Cohn W. E., ed.), vol. 18, p. 151 (1976).
7. Brabec V., Dryhurst G.: J. Electroanal. Chem. *89*, 161 (1978).
8. Palecek E., Lukásová E., Jelen F., Vojtísková M.: Bioelectrochem. Bioenerg. *8,* 497 (1981).
   Trefulka M., Ostatna V., Havran L., Fojta M., Palecek E.: Electroanalysis *19,* 1281 (2007) (and references therein).
9. Palecek E., Postbieglová I.: J. Electroanal. Chem. *214*, 359 (1986).
   Palecek E.: Bioelectrochem. Bioenerg. *20*, 171 (1988).
10. Palecek E.: Electroanalysis *8,* 7 (1996).
    Palecek E., Fojta M.: Anal. Chem. *73,* 74A (2001).
11. Palecek E., Jelen F.: Crit. Rev. Anal. Chem. *32*, 261

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* A year before the Nobel Prize was awarded to J. Heyrovský (Prague, Czechoslovakia) for polarography.

** The method introduced by J. Heyrovský to whom I am indebted for advice and support.

(2002).
Palecek E.: Talanta *56,* 809 (2002).
Drummond T. G., Hill M. G., Barton J. K.: Nat. Biotechnol. *21*, 1192 (2003).
Palecek E.: Trends Biotechnol. *22*, 55 (2004).
Wang J.: Anal. Chim. Acta *469*, 63 (2002).
Palecek E., Fojta M.: Talanta *74*, 246 (2007).
12. Palecek E., Scheller F., Wang J. (ed.): *Electrochemistry of Nucleic Acids and Proteins. Towards Electrochemical Sensors for Genomics and Proteomics.* p. 789. Elsevier, Amsterdam 2005.

## OP55

## APPLICATION OF ROOM TEMPERATURE IONIC LIQUIDS AS ELECTROLYTES IN ELECTROCHEMICAL SYSTEMS

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Organic electrolytes – room temperature ionic liquids (RTIL) – are usually organic or mixed organic-inorganic salts with a melting point lower than 100 ºC. In the last few years RTILs have become attractive in different fields such as catalysis, fundamental electrochemical studies of organic and inorganic compounds, formation of metal nanostructures, and in analytical and ioanalytical chemistry, including sensors and biosensors[1].

Carbon film electrodes have been extensively studied in aqueous solutions, after electrochemical pre-treatment usually exhibiting similar electrochemical properties to glassy carbon. Here, these electrodes have been characterised in the room temperature ionic liquids, 1-butyl-3-methylimidazolium bis (trifluoromethane)sulfonimide ($BmimNTF_2$), 1-butyl-1-methylpyrrolidinium bis(trifluoromethane)sulfonimide, ($BpyrNTF_2$) and 1-butyl-3-methylimidazolium nitrate ($BmimNO_3$), by cyclic voltammetry and electrochemical impedance spectroscopy. It was demonstrated that the electrochemical behaviour depended on both cation and anion of these ionic liquids. Oxygen reduction is clearly visible at carbon film electrodes – after oxygen removal the potential window was wider[2].

The application of these room temperature ionic liquids will be demonstrated and discussed. These RTILs were used in the electrochemical investigation of two ferrocene derivatives, benzoyl- and acetyl-ferrocene, that are both insoluble in water and of two sensor and biosensor mediators, copper hexacyanoferrate and poly(neutral red), with a view to using ionic liquids as electrolytes in electrochemical sensing and biosensing systems[2]. $BmimNO_3$ has been successfully applied in a glucose biosensing system[3].

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REFERENCES

1. Wei D., Ivaska A.: Anal. Chim. Acta *607*, 126 (2008).
2. Pauliukaite R., Doherty A. P., Murnaghan K. D., Brett C. M. A.: J. Electroanal. Chem., in press.
3. Pauliukaite R., Doherty A. P., Murnaghan K. D., Brett C. M. A.: Electroanalysis, in press.

## OP56

## GATE EFFECT OF MOLECULAR IMPRINTED POLYMERIC MEMBRANES FOR SPECIFIC SENSORS

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Molecular imprinted polymers (MIP) have molecular recognition properties similar to those of natural receptors, with good recognition ability and specificity. They are widely used as recognition elements in sensors with electrochemical transduction, as reported for example by Piletsky and Turner[1]. MIPs for selected template substances have been previously prepared as omogeneous thick membranes with mechanical properties suitable to obtain a potentiometric ISE sensor[2]. Here the same kind of membrane is tested for the possibility of taking advantage of its gate effect[3]. To this aim the signal measured is a faradic current modulated by the rebinding of the template molecule to the MIP membrane. The electroactive substance responsible for the current signal can be different from the template molecule, so that the method can be used for the detection of not electroactive substances.

For demonstrating this possibility an amperometric sensor for isopropyl-thioxanthen-9-one (ITX), which is not electroactive on carbon electrodes, was prepared based on the gate effect. A thick molecularly imprinted polymeric (MIP) membrane (0.6 μm thickness) was directly formed on a graphite electrode of 0.5 mm diameter (MIP-GE). This was the working electrode in a three electrode cell in which the current was measured at -850 mV (*vs.* Ag/AgCl sat). The solution was Britton-Robinson buffer at pH 1.5. The current is due to the reduction of $H^+$ ions. It has been found to linearly depend on the concentration of the template molecule, decreasing with the concentration of ITX. A similar effect was observed in the case of other hydrophobic templates, while in the case of more polar templates, as for instance atrazine, the current intensity increases with the concentration. The detection limit at the considered conditions was $9\times10^{-7}$ M for ITX. A number of molecules of similar structure were considered to test the selectivity, demonstrating that the gate effect of the MIP membrane is very specific for the template. A current was obtained both on bare carbon electrodes, and on electrodes covered with a non imprinted membrane (NIP) of similar composition, but only in the case of MIP-GE it does not vary with the template concentration. Evidently the gate effect depends on the specific nanocavities which act as selective receptors for the corresponding template and at the same time as modulators of the current.

REFERENCES
1. Piletsky S. A., Turner A. P. F.: Electroanalysis *14*, 317 (2002).
2. D'Agostino G., Alberti G., Biesuz R., Pesavento M.: Biosens. Bioelectron. *22*, 145 (2006).
3. Yoshimi Y., Odhaira R., Iiyama C., Sakai K.: Sens. Actuators, B *73*, 49 (2001).

## OP57

## MULTI-FUNCTIONAL ELECTRODE ARRAYS: TOWARDS A UNIVERSAL DETECTION PLATFORM

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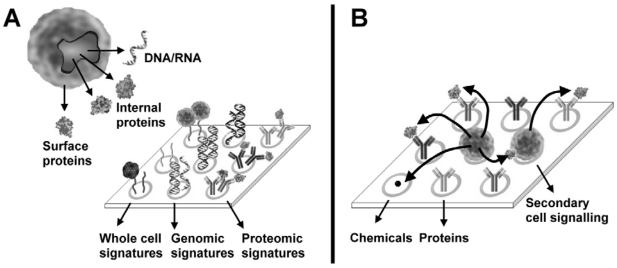
In order to improve the efficiency of array technology it is desirable to perform multi-target assays on the same platform which greatly increases the throughput and the amount of information that can be obtained in a single assay. Normally these sensor arrays require separate platforms for analysis. The detection of pathogens, such as anthrax, would benefit from the ability to detect genomic, proteomic, and whole-cell signatures which would reduce false positive measurements and increase confidence in the sensors results. Herein we present recent work in our laboratory towards the realization of a multianalyte microelectrode detection platform capable of discriminating chemicals and different biomolecules simultaneously. The functionalization of electrodes with aryl diazonium salts provides an electrically addressable deposition procedure capable of immobilizing a wide range of molecules. We demonstrate control over surface density and electron transfer kinetics as well as the activation of individual electrodes in an array. The direct electrically-addressable immobilization of diazonium-modified proteins is shown to be suitable for the construction of multianalyte immunosensors and the immobilization of horseradish peroxidase leading to the direct electron transfer between the redox enzyme and the electrode. The use of catalytic nanoparticles leads to the construction of a reagent-less immunosensor and the simultaneous detection of DNA and proteins on the same electrode array is demonstrated.

New immobilization procedures which increase the stability of biomolecules may lead to the introduction of multi-sensor systems for simultaneous monitoring of both biological and chemical events. For example, cells can release a combination of proteins and small molecules upon exposure to particular stimuli, presented in Fig. A. Many cell-cell and host-pathogen interactions undergo a cascade of events that require complex detection strategies to elucidate mechanisms and signaling pathways. We are currently testing the feasibility of diazonium chemistry conjugated with boronic acid to capture live cells on electrodes. As shown in Fig. B, it may be possible to detect changes in membrane conductance and release of electroactive chemicals while monitoring the release of cytokines involved in secondary signaling. The ability to perform electrochemical experiments in microfluidic systems opens up many new opportunities for synthesis and sensing applications.



## OP58

## CARBON NANOPARTICLE-CHITOSAN THIN FILM ELECTRODES: FORMATION, CHARACTERIZATION, AND ANALYTICAL APPLICATIONS

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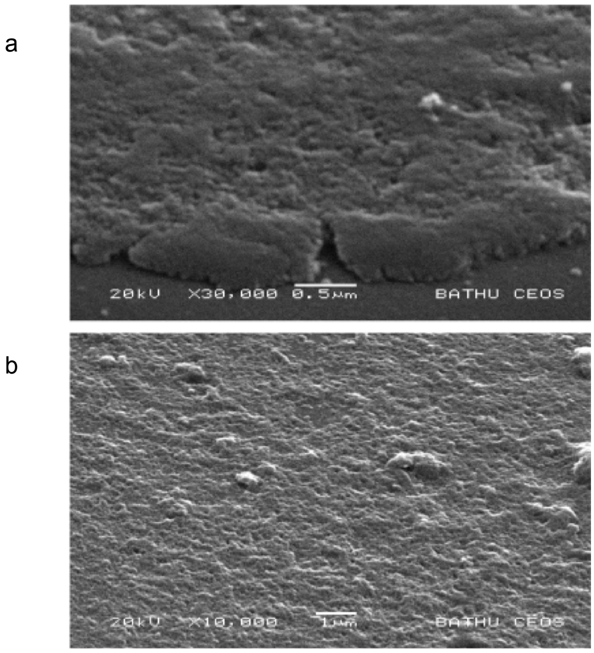
Hydrophilic carbon nanoparticles similar to metal nanoparticles are very interesting building blocks in thin film electrode systems and their high surface area and high level of interfacial edge sites are potentially beneficial in electrochemical processes[1]. Chitosan (used here as a binder for hydrophilic carbon nanoparticles) is a cationic polyelectrolyte (p$K_a$≈6.5), soluble in aqueous acidic media, which forms water insoluble complexes for example with anionic poly electrolytes. Chitosan as an environment-friendly and cost-effective material, has received considerable interest in recent years in particular for the removal of heavy metals[2–5]. The nanocomposite carbon nanoparticle-chitosan film electrode is subject of this contribution and can be obtained with different experimental methods including layer by layer formation or solvent evaporation.

In this study, chitosan (poly-D-glucose-amine) has a dual effect as (a) the binder for the mesoporous carbon composite structure and as (b) binding site for redox active probes and metal ions. Physisorption onto the positively charged ammonium group occurs for example with indigo carmine which undergoes a reversible $2e^- - 2H^+$ reduction in aqueous media. Chemisorption at the amine functionalities is demonstrated with 2-bromo-methyl-anthraquinone which also undergoes a reversible $2e^- - 2H^+$ reduction in aqueous media. It is possible to control the number of binding sites and porosity in the film with the chitosan concentration during film formation. Chitosan – carbon nanoparticle composite electrodes are shown to effectively bind mercury. Once immobilised, the



Scheme 1. **SEM images for (a) a 2-layer chitosan-carbon nanoparticle film and (b) the porous topography of the surface for a 4-layer chitosan-carbon nanoparticle deposit**

mercury is permanently fixed within the nanocomposite and it is demonstrated that the resulting electrode is effective as a mercury electrode replacement.

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REFERENCES

1. Banks C. E., Compton R. G.: Anal. Sci. *21*, 1263 (2005).
2. Kubota N., Kikuchi Y.: *Macromolecular Complexes of chitosan*. (Dumitriu S., ed.). Polysaccharides, p. 595. Dekker, New York 1998.
3. Chu K. H.: J. Hazard. Mater. B *90* ,77 (2002).
4. Onsoyen E., Skaugrud O.: J. Chem. Technol. Biotechnol. *49*, 395 (1990).
5. Vieira R. S., Beppu M. M. : Colloids Surf., A *279*, 196 (2006).

## OP59

## HYBRID MICROFLUIDIC SENSORS FABRICATED BY SCREEN PRINTING AND INJECTION MOULDING FOR ELECTROCHEMICAL AND ELECTROCHEMILUMINESCENCE DETECTION

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An integrated microfluidics / electrochemical sensor with dual working electrode configuration was fabricated for voltammetric and electrochemiluminescence (ECL) applications. The fabrication method is based on the integration of two techniques: injection moulding and the screen printing. The former is used for the generation of the base plate of the flow cell containing the electrical connectors, and the top plate, containing the flow channel and the fluidic connectors. Screen printing is used for printing the electrodes directly on the injection moulded base plate. An over moulding procedure followed by ultrasonic welding was used to form the complete sensor. High impact polystyrene (HIPS), Zeonor® and SAN materials were evaluated for their compatibility with screen printing. Among those, Zeonor® gave the best results and thus was selected for the flow cell fabrication. An interdigitated working electrodes design with 200 µm width and spacing was successfully printed using carbon ink, platinaised carbon ink or both. Planar reference and counter electrodes were also printed on the base plate using Ag/AgCl and carbon inks respectively.

The electrochemical and ECL performance of the sensors were assessed by applying different electrochemical methods such as cyclic voltammetry, anodic stripping voltammetry and chronoamperometry. The attractive analytical performance demonstrates good capability of the disposable sensors for routine on-line electrochemical and ECL measurements.

## OP60

## ELECTRON TRANSFER AT THE LIQUID-LIQUID INTERFACE AND FACILITATED PROTON TRANSFER INDUCED BY A DISPROPORTIONATION REACTION

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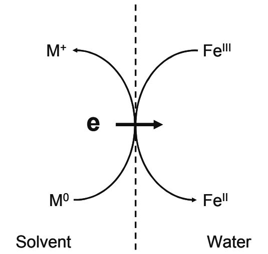
Electron transfer across the water/dichlorohexane liquid/liquid interface has been studied with $Fe^{III/II}$ hexacyanoferrate in the aqueous phase and a lutetium bisphthalocyanine in the solvent ($M^0$) :



$$Fe^{III}_{w} + M^{0}_{s} \Leftrightarrow Fe^{II}_{w} + M^{+}_{s}$$

Scheme 1. **Electron transfer at a liquid/liquid interface**

Lutetium bisphthalocyanines are much better candidates than ferrocenes for such studies because of their total insolubility in water and of their chemical stability[1,2]. Moreover, they can be oxidized as well as reduced. The electron exchange has been studied by voltammetry at a liquid/liquid microinterface. It has been noticed during investigations that the proton transfer from water to nitrobenzene or dichlorohexane was facilitated by the presence of the lutetium bisphthalocyanine in the solvent and by its disproportionation reaction[3]:

$$2\ M^0{}_s + H^+{}_w \leftrightarrow M^+{}_s + HM_s$$

Proton is a highly hydrophilic ion but its transfer is much easier, by almost 30 kJ mol$^{-1}$, due to the protonation reaction of M$^-$, the reduced bisphtalocyanine. This has been investigated by voltammetry under stationary conditions at the microinterface between the two immiscible liquid media.

REFERENCES

1. Njanja E., Nassi A., Ngameni E., Elleouet C., Quentel F., L'Her M.: Electrochem. Commun. *9*, 1695 (2007).
2. L'Her M., Rousseau R., L'Hostis E., Roue L., Laouénan A.: C. R. Acad. Sci. Paris, série IIb, *322*, 55 (1996).
3. L'Her M., Cozien Y., Courtot-Coupez J.: C. R. Acad. Sci. Paris, série II, *300*, 487 (1985).

## OP61

## APPLICATION OF NANOMETER THICK MERCURY FILM ELECTRODES IN THE DYNAMIC SPECIATION FEATURES OF METAL COMPLEXES, BY SCANNED STRIPPING CHRONOPOTENTIOMETRY

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In natural waters, metal ions are usually distributed over a variety of complexes with dissolved ligands and dispersed particles, spanning a range of complex stabilities and labilities. Understanding the bioavailability of metal species requires consideration of the overall flux towards the organism surface, which arises from the coupled diffusion and association/dissociation kinetics involving the various metal species in the medium. The contribution of dynamic complexes depends on the relative magnitude of the diffusive and kinetic fluxes and will range from fully labile (diffusion controlled) to non labile (kinetic controlled)[1,2].

Scanned stripping chronopotentiometry (SSCP) curves, i.e. plots of the transition time (SCP analytical signal) *vs*. the applied deposition potential, are inherently rich in information, providing data on the stability distribution spectrum and, if applicable, on the corresponding fraction of the rate constant distributions. Recently, thin mercury film electrodes (TMFE) plated onto glassy carbon proved to be an excellent complement to the conventional mercury electrodes (hanging mercury drop electrode and the Hg-Ir microelectrode) in the construction of SSCP experimental waves, due to the high sensitivity and resolution as well as to the low deposition times which are used[3].

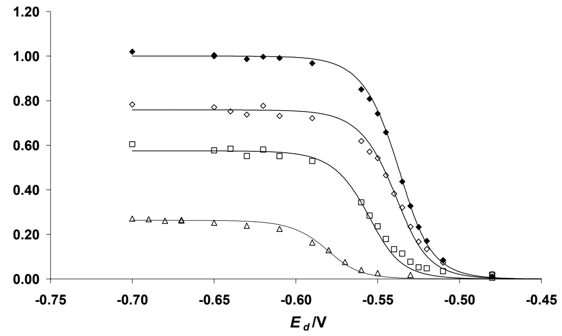

Fig. 1. **Experimental and fitted SSCP waves for Pb and Pb-IDA at pH 5.5 for the TMFE** (thickness of 8 nm). Experimental curves were measured for 1.2×10$^{-7}$ mol dm$^{-3}$ Pb(II) in 0.01 NaNO$_3$ mol dm$^{-3}$ in the absence (♦) and presence of IDA: 2.4×10$^{-5}$ mol dm$^{-3}$ (◊), 3.8×10$^{-4}$ mol dm$^{-3}$ and (□), 2.8×10$^{-3}$ mol dm$^{-3}$ (∆). Other experimental conditions: td = 80 s and Is = 7.5×10$^{-8}$ A. Fitted waves (full line)

The present work explores further the potentialities of the TMFE in SSCP dynamic speciation studies to fully take advantage of the well defined hydrodynamic features of this electrode. The characteristic parameters of the SSCP wave (the limiting wave height, $\tau^*$, and the half-wave deposition potential, $\Delta E_{d,1/2}$) provide a sensitive indicator of the loss of lability in metal complex systems[1,2].

The system lead(II)–iminodiacetic acid (Pb-IDA) complex was used to evaluate the potential of SSCP for the determination of the association rate constant, $k_a$, in the kinetic current regime. With increasing ligand concentration, there was a decrease in $\tau^*$ and a shift of $E_{d,1/2}$ towards negative potentials (Fig. 1), indicating a loss of lability of the system. For each ligand concentration the both value of the association rate constant, $k_a$ and the stability constant, $K$, were determined and compared with the published values.

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REFERENCES

1. Pinheiro J. P., van Leeuwen H. P.: J. Electroanal. Chem. *570*, 69 (2004).
2. van Leeuwen H. P., Raewyn M. Town: J. Electroanal. Chem. *561*, 67 (2004).
3. Rocha L. S., Pinheiro J. P., Carapuça H. M.: J. Electroanal. Chem. *610*, 37 (2007).

## OP62

# STUDY OF REDUCTION AND OXIDATION OF HETEROPOLYANIONS USING POTENTIOMETRIC CHEMICAL SENSORS

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The present research was aimed at the application of an array of potentiometric chemical sensors to the study of the mechanism of the reduction and oxidation of some polyoxometalate (POM) complexes. Phosphovanadomolibdates of the Keggin-type and formulae $[PMo_xV_{12-x}O_{40}]^{(3+x)-}$ were chosen for this study as compounds that have been extensively studied as catalysts for the oxidation of several types of organic substrates, including delignification of lignocellulosic materials. In the catalytic process it is assumed that the substrate is oxidized while the V(V) atoms in the POM structure are reduced to V(IV) followed by re-oxidation of vanadium centers in POM by $O_2$. It is of some controversy if reduction and oxidation of vanadium occur inside the Keggin-type structure of POM or outside. If it does, a mixture of POM in oxidized and reduced forms and of vanadium outside POM as $VO^{2+}$ and $VO_2^+$, or other species would be present in the solution. Therefore, an analytical technique capable of measuring these vanadium species in solution in the real time is necessary for elucidation of the mechanism of these reactions.

Methods that are conventionally used for the detection of V(IV) (EPR spectroscopy) or V(V) ($^{51}V$ and $^{31}P$ NMR) species in solutions are not suitable for their simultaneous and instantaneous determination. It was demonstrated that simultaneous detection of V(IV) and V(V) species in the aqueous solutions can be carried out using is an array of potentiometric chemical sensors[1].

In the present work an array of sensors was applied to the real-time follow-up of the changes of the concentrations of vanadium containing species in the course of the reduction and re-oxidation of the phosphovanadomolibdates containing one and two vanadium atoms. Sensors displaying red-ox sensitivity and sensitivity to V(IV), V(V) and vanadium containing POM were chosen based on the previous work[1]. Changes of the species concentrations during reduction of the POM and their re-oxidation by air and in the presence of catalyst – laccase were monitored using sensor array. Mechanism of POM re-oxidation was suggested based on the observed changes in the concentrations of vanadium containing species.

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REFERENCE

1. Rudnitskaya A., Evtuguin D. V., Gamelas J. A. F., Legin A.: Talanta *72*, 497 (2007).

## OP63

# ELECTROCHEMICAL METHODS FOR THE INVESTIGATION OF BIOAFFINITY INTERACTIONS

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An approach based on volt-amperes' characteristics of voltammograms and amperograms for the analysis of substrate specificity of cytochromes P450 was proposed. To obtain nanoelectrode systems, based on gold nanoparticles on the electrode surface we used colloidal Au solution stabilized with lyotropic liquid crystalline phase of membrane-like synthetic surfactant didodecyldimethylammonium bromide DDAB. The electrochemical behavior of nanostructured electrodes with immobilized cytochromes P450 2B4, 1A2, 3A4, 11A1 (P450scc), and 51b1 (sterol 14α-demethylase, CYP51b1) in the presence of typical substrates and inhibitors of these forms were studied. Based on the results of amperometry, cyclic voltammetry, voltammetric analysis (DPV and SWV) and intermittent pulse amperometry (IPA), it was possible to conduct a search and to study the kinetic parameters of potential substrates and inhibitors of cytochrome P450. The proposed electrochemical approach is a sort of a bio-bar code of cytochrome P450 for the determination of the substrate/inhibitor P450's competence. The method of electro analysis may be applied to creation of multichannel electrochemical plates (chips, panels) with immobilized cytochromes P450.

A novel electrochemical method for the detection of bioaffinity interactions based on a gold nanoparticles sensing platform was developed. Voltammetric method for a direct determination of gold nanoparticles based on stripping voltammetry of Au/Au oxides film was studied. The sensor signal was a gold oxides reduction peak current after 30 s oxidation, $E = +1.2$ V. The surface characteristics of the composite electrodes were investigated for the detection of myoglobin – antibody or thrombin – aptamer interactions.

*This work was supported by the Federal Agency of Science and Innovations, Ministry of Education and Science of the Russian Federation (State contract № 02.512.11.2105) and by the Interdepartmental Program "Proteomics in Medicine and Biotechnology".*

REFERENCES

1. Shumyantseva V. V., Bulko T. V, Rudakov Yu. O., Kuznetsova G. P., Samenkova N. F., Lisitsa A. V., Karuzina I. I., Archakov A. I.: Biochemistry (Moscow) Supplement Series B: Biomedical Chemistry *1*, 327 (2007).
2. Shumyantseva V. V., Bulko T. V, Rudakov Yu. O., Kuznetsova G. P., Samenkova N. F., Lisitsa A. V., Karuzina I. I., Archakov A. I.: J. Inorg. Biochem. *101*, 859 (2007).

## OP64

## COMPOUNDS INCLUDED GUANIDINE GROUP AS CATALYSTS FOR HYDROGEN REDUCTION AT A MERCURY ELECTRODE: APPLICATION IN ANALYSIS OF PHARMACEUTICLS IN BIOLOGICAL SAMPLES

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It was stated that some organic substances including guanidine group like famotidine, metformin, aciclovir, ganciclovir, 2-guanidinebenzimidazol can catalyze effectively the hydrogen evolution reaction. They can be considered as a new group of catalysts in the catalytic systems of hydrogen ions. New square-wave voltammetric (SWV) methods of famotidine[1] metformin[2] and acyclovir[3] determination based on the hydrogen evolution reaction catalyzed by adsorbed catalyst at the CGMDE were developed. We analyzed both theoretically and experimentally under conditions of SWV the electrode mechanism of famotidine[4] and metformin[2]. Each of the mentioned compounds as the adsorbed catalyst is undergoing protonation at the electrode surface, the protonated form of the catalyst is irreversibly reduced yielding the initial form of the catalyst and atomic hydrogen. It is in accordance with the schemes of catalytic reactions[5] .The most important advantage of the presented studies arises from the fact that the inactive at mercury electrode compounds act as electrocatalysts and can be determined by voltammetric methods. The voltammetric procedures were characterized with respect to the repeatability, precision and the recovery. The detection and quantification limits respectively were found to be: $4.9\times10^{-11}$ $L^{-1}$ and $1.6\times10^{-10}$ $L^{-1}$ for famotidine (SW AdSV), $1.8\times10^{-8}$ $L^{-1}$ and $5.9\times10^{-8}$ $L^{-1}$ for metformine (SW AdV), $7\times10^{-8}$ $L^{-1}$ and $2\times10^{-7}$ $L^{-1}$ for acyclovir (SWV). The SW voltammetric method was applied for direct determination of famotidine and metformin in human urine.The method has been validated by using HPLC with UV detection.

### REFERENCES

1. Skrzypek S., Ciesielski W., Sokołowski A., Yilmaz S., Kaźmierczak D.: Talanta *66*, 1146 (2005).
2. Skrzypek S., Mirceski V., Ciesielski W., Sokołowski A., Zakrzewski R.: J. Pharmaceut. Biomed. Anal. *45*, 275 (2007).
3. Skrzypek S., Ciesielski W., Yilmaz S.: Chem. Anal. (Warsaw) *52* (2007).
4. Mirceski V., Skrzypek S., Ciesielski W., Sokołowski A.: J. Electroanal. Chem. *97*, 585 (2005).
5. Bobrowski A., Zarębski J.: Electroanalysis *12*, 1177 (2000).

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## OP65

## ELECTROCHEMICAL SENSING OF GLYPHOSATE AND AMINOMETHYLPHOSPHONIC ACID USING NANOCOMPOSITE POLYMER-ON-GOLD NANOBIOSENSOR

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The increasing number of potentially harmful pollutants in the environment calls for fast and cost-effective analytical techniques to be used in extensive monitoring programs. The requirements, both in terms of time and costs, of most traditional analytical methods (e.g. chromatographic methods) often constitute an important impediment for their application on regular basis. In this context, biosensors appear as suitable alternative or complementary analytical tools. This study presents the development of a simple, sensitive, rapid and low cost amperometric nanobiosensor for quantitative determination of the herbicide glyphosate and its metabolite aminomethylphosphonic acid (AMPA). The nanocomposite film composed of poly(2,5-dimethoxyaniline) (PDMA) and poly (4-styrenesulfonic acid) (PSS) nanoparticles was successfully prepared by electropolymerization on the surface of a rotating gold disk electrode. It was characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and subtractively normalized interfacial FTIR (SNIFTIR) spectrophotometer. The functionalized film was characterized by fast charge propagation, and it served as a redox conducting template for attachment of a model enzyme, horseradish peroxidase, HRP. The resulting nanobiosensor was applied for electrochemical sensing of glyphosate and AMPA in soya bean samples. Hydrogen peroxide was used to measure activity of the enzyme before injection of the herbicides into the electrolyte solution. Glyphosate and AMPA analyses were realized on spiked soya bean samples within a concentration range of 2.0–78.0 $\mu g\ L^{-1}$ and with recovering percentages close to 100 %, corroborating that the nanobiosensor is sensitive enough to detect the herbicides in these matrices. Based on a 20 µL sample injection volume, the detection limits were 0.1 $\mu g\ L^{-1}$ ($10^{-10}$ M) for both glyphosate and AMPA without sample clean-up or preconcentration.

*Financial support from Third World Organization for Women in Science (TWOWS) and National Research Foundation (NRF), South Africa is gratefully acknowledged.*

## OP66

## ADVANCED DESIGN OF A BIOFUEL CELL USING LACTOSE/CELLOBIOSE AS FUEL FOR ANODE

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In the last years, the description of various designs of biofuel cell architectures was aiming at the use of a variety of environmental friendly fuels such as hydrogen, organic acids, alcohol, sugars. Such fuels might be considered for providing energy in a biofuel cell by integration of complementary biocomponents, such as enzymes, microbial or whole cells for catalyzing the reactions at the anode and/or cathode.

In order to fulfil the high efficiency standards required for a biofuel cell, one shall take in consideration a multitude of parameters regarding the integrated biocomponent: *e.g.* its loa-ding, operational stability, design of efficient electron-transfer pathways between biocomponent and electrode (anode/ca-thode), enhanced active area of electrode, etc.

Here, cellobiose dehydrogenase was involved in catalytically "burning" (oxidation) of lactose/cellobiose fuels at the anode side, in combination with a cathode on which lacasse was responsible for oxygen reduction at high formal potentials. The principle feasibility of combining two modified electrodes as anode and ca-thode within a biofuel cell is demon-strated in Figure 1.

This initial proof of the functioning principle was now further opti-mized with respect to biofuel cell potential, enzymes loading and active areas of the electrodes. This was achieved by using specifically designed of Os-complex modified redox polymers that are able, in the case of cellobiose dehydrogenase, to specifically pick-up electrons from the FAD-subdomain and, as a consequence, by-passing the contribution of the heme-subdomain in the electron transfer pathway, resulting in a negative shift of 200 mV for the anode side. For the cathode side, a different polymer was designed for opti-mum electron transfer at high potentials (~500 mV *vs.* Ag/AgCl). The redox polymers were in addition supporting a high loading with enzymes on both electrodes. Moreover, an efficient electric wiring of the polymer-bound Os-centres from the vicinity of the biocomponent to the electrode surface was achieved by using an advanced electrode architecture based on highly conducting hierarchical two-generation carbon micro-/nanotubes as drawn in Figure 2 (ref.[1]).

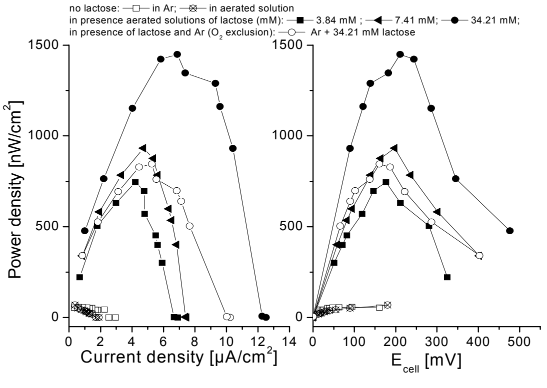

Fig. 1. **Initial power density of CDH/lacasse biofuel cell in respect to current density and cell potential**

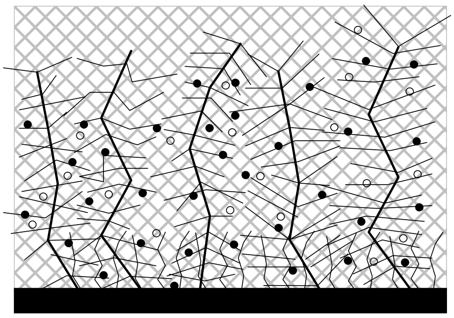

Fig. 2. **Schematic representation of hierarchical two-generation carbon micro-/nanotube structure as anode with an enlarged active surface area for enzyme loading (○) and improved wiring via Os-containing redox polymer (●)**

The optimized biofuel cell design along with the obtained results concerning cell-power, operational stability will be discussed.

REFERENCES

1. Nan L., Chen X., Stoica L., Xia W., Qian J., Aßmann J., Schuhmann W., Muhler M.: Adv. Mater. *19*, 2957 (2007).

## OP67

## ELECTRODES MODIFIED WITH SINGLE-WALLED CARBON NANOTUBES FOR APPLICATIONS IN BIOSENSORS, BIOFUEL CELLS AND FOR ELECTROCHEMICAL STUDIES OF REDOX ENZYMES

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In recent years single-walled carbon nanotubes (SWCNTs) have been used to promote the electrochemical communication between electrodes and redox enzymes.

Whereas most frequently the SWCNTs have been used without purification and further characterization, there might be large differences in quality, morphology, and length of the SWCNTs which can have strong influence on the performance of the nanotubes during bioelectrochemical applications. We have oxidatively shortened, purified, and separated SWCNTs with respect to their average length by size exclusion chromatography. The different fractions were characterized by means of microscopic techniques such as high resolution transmission electron microscopy, cryogenic transmission electron microscopy and atomic force microscopy.

Individual fractions of these nanotubes were compared with respect to their ability to improve the electrochemical communication between electrode and redox enzymes. In particular the enzymes cellobiose dehydrogenases (CDHs), pyranose dehydrogenase, diaphorase, and tryptophan repressor binding protein (WrbA), have been studied. Different electrode architectures were compared. The SWCNTs were able to increase the rate of direct and mediated electron transfer whereupon a strong influence of the average length of the SWCNTs on the electrocatalytic current was observed. The enzyme/SWCNT modified electrodes were employed in amperometric biosensors and biofuel cells.

## OP68

## VISUALISATION OF THE LOCAL CATALYTIC ACTIVITY OF Pt ALLOY CATALYST FOR OXYGEN REDUCTION USING SCANNING ELECTROCHE-MICAL MICROSCOPY

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Pt-Ag nanoparticles catalysts with different concentration ratio were prepared on a glassy carbon electrode surface by a pulsed electrodeposition method and investigated with respect to their catalytic activity for oxygen reduction (ORR)[1] for potential applications in proton exchange membrane fuel cell (PEMFC). The atomic composition was studied by means of energy dispersive X-ray diffraction ana-lysis (EDAX) which confirms the presence of Pt and Ag on the surface, while the morphology was investigated by scanning electron microscopy (SEM). SEM images indicated that the prepared catalyst partic-les are homogenously dispersed on the surface with a particle size of typically 20–40 nm (Figure 1).

The catalytic properties of the prepared catalyst with respect to ORR were evaluated using cyclic voltammetry in phosphate buffer. A comparative study was made using a rotating disk electrode to evaluate the catalytic behaviour of Pt-Ag deposits with different metal loading. The observation confirms that the codeposited amount of Ag is an important parameter for fine-tuning of the catalytic activities of bimetallic nanoclusters. If true alloying occurred during the electroche-mical deposition the observed enhancement may originate from favourable electronic effects of a well mixed alloy. Redox competition mode scanning electrochemical microscopic (RC-SECM)[2] studies were carried out to visualize the local catalytic activity of Pt-Ag nanoparticles in phosphate buffer after formation of catalyst spots using a micro droplet cell (Figure 2a). Figure 2b clearly demonstrates the catalytic activity of the deposited Pt-Ag nanoparticles.

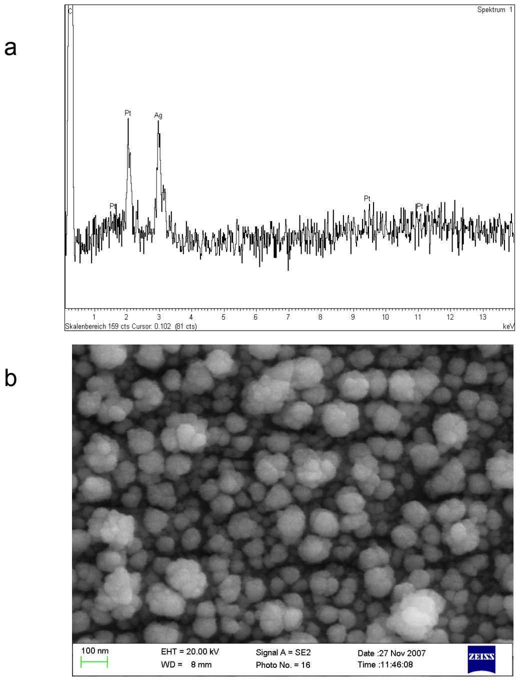

Fig. 1. (a) **Energy dispersive X-ray diffraction analysis and** (b) **scanning electron micrograph of Pt-Ag catalyst deposited on glassy carbon**

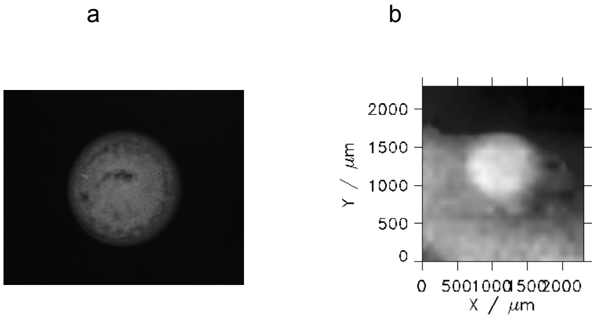

Fig. 2. (a) **Catalyst picture and** (b) **visualized catalyst spot by RC-SECM in phosphate buffer**

REFERENCES

1. Hwang B. J., Senthil Kumar S. M., Chen C.-H., Monalisa

C., Ming-Yao, Liu D.-G., Lee J.-F.: J. Phys. Chem., C *111*, 15267 (2007).
2. Eckhard K., Chen X., Turcu F., Schuhmann W.: Phys. Chem. Chem. Phys. *8*, 5359 (2006).

## OP69
## INDIRECT VOLTAMMETRIC DETERMINATION OF FLUORIDE IONS ON INTERDIGITATED MICROELECTRODE ARRAY

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A novel method for the detection of fluorides based on dynamic electrochemistry is presented. Fluoride anion is an important component of food product as well as environmental samples. In practical analysis mainly potentiometric method based on ionselective electrodes is used. Potentiometric response, however, is logarithmic function of concentration. Its antilogarithmization for obtaining concentration causes large error. The proposed voltammetric method is based on electroinactivation of iron (III) by strong complexation with fluoride under formation hexafluoroferric ion. Diffusion current of iron(III) is thus decreased when fluorides are added to the solution. The response of noncomplexed iron was registered by cyclic voltammetry and by constant potential amperometry measuring iron(III) reduction current. In both methods the determination limit of $10^{-4}$ M was obtained on platinum interdigitated microelectrode array (IDA). The determination limit is one order lower than in the case of classic amperometric (polarometric) titration on platinum macroelectrode[1]. This is due to diffusion layer overlapping of electrode digits[2]. The capacity current is reduced. In addition the dimensions of IDA chip opens the possibility of microanalytical determination of fluorides.

*This work was suopported by the Slovak Research and Development Agency under the contract No. APVV-0057-06.*

REFERENCES
1. Doležal J., Zýka J., in: *Polarometric Titrations*, Chap. II, p. 42. Státní nakladatelství technické literatury, Prague 1961.
2. Tomčík P., Jenčušová P., Krajčíková M., Bustin D., Manová A., Čakrt M.: J. Electroanal. Chem. *593*, 167 (2006).

## OP70
## FORMATION AND IMAGING OF GRADIENTS IN ELECTROCHEMICAL REACTIONS AND MOLECULAR FILMS

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One limitation with standard electrochemical experiments is that the potential difference between the electrode and solution is basically the same for the entire interface. Also, based on the current, it is difficult to separately evaluate faradaic reactions on different parts of the electrode surface. This presentation will describe the use of electric fields and bipolar electrodes to generate gradients in electrochemical reactions on gold surfaces, and the use of imaging optics for evaluation of such gradients. The major advantages with this approach are that gradients in for example surface modifications can be formed relatively quickly, and that the surfaces themselves do not have to be contacted by electric wires[1].

As shown in Fig. 1, a voltage (or current) source and two electrodes are used to electrochemically induce an electric field in a solution in which a conducting surface is placed. The latter surface can then become a bipolar electrode, i.e. an electrode acting both as an anode and cathode, as it offers a less resistive path for the current. This occurs when the electric field parallel to the surface becomes sufficiently high to induce redox reactions at both ends of the surface. In the present approach, a potential gradient across the electrode is thus induced by the electric field in the solution rather than by controlling the potential of the electrode. Since the potential difference between a point on the bipolar electrode and the solution will vary laterally along the surface, the driving force for electrochemical reactions varies accordingly. The rate of redox reactions will be highest at the edges of the electrode, and decrease towards the center of the surface. As will be shown, this can be used to create a surface gradient of mo-

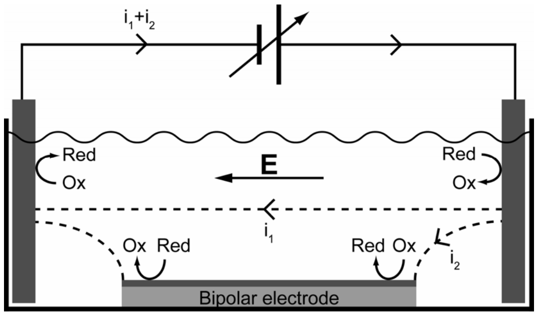

Fig. 1. **Schematic experimental setup, showing the current paths when electrochemical reactions take place on the bipolar electrode**. A variable voltage source is used to control the total current between e.g. two stainless steel electrodes

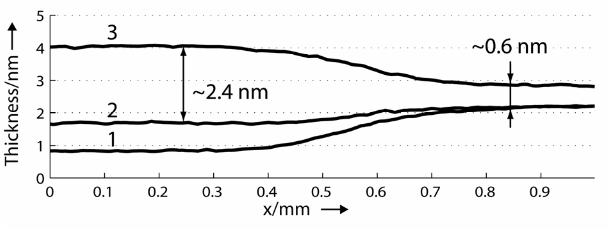

Fig. 2. **Line profiles from imaging ellipsometry measurements showing the thicknesses after the different preparation steps of the protein gradient**. Line 1 shows the result of the desorption of mPEG, line 2 the result after the backfilling with aPEG, and line 3 the resulting protein gradient. The bare gold parts were contaminated by hydrocarbons from the air during the ellipsometric analysis (corresponding to ca. 0.8 nm for line 1)

lecular functionality since bipolar electrode reactions can be used to control the adsorption or desorption of a specific molecule.

The faradaic reactions on the bipolar electrode were visualized via imaging Surface Plasmon Resonance (iSPR). This detection method is based on changes in the refractive index of the solution in a region very close to the surface (some 350 nm). By choosing a redox couple with different refractive indices for the oxidized and reduced forms, the extent of the faradaic reactions along the bipolar electrode can then be monitored. Cyclic and pulsed voltammetry have further been combined with the iSPR-instrumentation to demonstrate the extent of faradaic reactions on differents parts of a heterogeneously modified gold surface[2]. This is basically an instrumental combination for imaging of electrochemical reactions with a lateral resolution in the micrometer range.

Imaging ellipsometry has further been employed to provide thickness maps of gradients in molecular films (i.e. Self-Assembled Monolayers, SAMs). These gradients were formed by incubating SAMs on gold surfaces, and in the next step using the latter as bipolar electrodes as described in Fig. 1. This could also be used to produce molecular films with a gradient in immobilized proteins (Fig. 2). Briefly, a gradient of an inert thiol (mPEG) was formed, and the empty sites of the gold surface where then backfilled with a second carboxy-terminated thiol (aPEG). In the last step, the carboxy-groups were activated, and lysozyme could then be attached to the aPEG gradient. Such surfaces are, for example, very attractive when optimizing biochemical reactions on surfaces.

REFERENCES

1. Ulrich C., Andersson O., Nyholm L., Björefors F.: Angew. Chem. Int. Ed. Engl., in press.
2. Andersson O., Ulrich C., Björefors F., Liedberg B.: submitted.

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## OP71

## ENHANCEMENT OF AMPEROMETRIC SIGNALS BY MEANS OF HEATED SENSORS

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This communication reports about thermal modulation of amperometric signals by short heat pulses[1] and continuous heating applied at electrically heated electrodes. Electrodes tested include gold and platinum layers on low temperature cofired ceramic (LTCC) substrates as well as noble metal wires and carbon electrodes[2]. We chose hexacyanoferrate(II) and picric acid as model analytes to explore "Temperature Pulse Amperometry" in a preliminary study[1]. Here, peak-shaped amperometric signals were formed upon thermal modulation by short heat pulses. The peak current had been taken as the analytical information. Thermal modulation in amperometric measurements also activates kinetically inhibited analytes such as picric acid. A linear calibration plot has been obtained ranging from 0.2 to 1 mmol $l^{-1}$. The background contribution was effectively suppressed, even at −0.7 Volts applied potential at the gold electrode. Convection did not significantly affect the analytical signal. This will be important for applications where convection is pulsating or is otherwise not under control and thus induces disturbances.

Another great advantage of electrode heating is especially important for amperometric detectors. Electrode fouling can often be prevented by means of heated electrodes as we have demonstrated in the cases of NADH[4] and dopamine[5] detection.

A major step in the development of directly heated electrodes is a special filtering device. The high power heating current can effectively be separated from the electrochemical signals by means of an inductor bridge[2,3]. This way, even electrode materials with a high resistivity such as carbon can be heated simultaneously to the electrochemical measurements[2].

Future applications include environmental monitoring, flow injection analysis, high performance liquid chromatography and capillary electrophoresis.

*The authors are grateful to the Deutsche Forschungsgemeinschaft and the State of Mecklenburg-Vorpommern for financial support.*

REFERENCES

1. Wachholz F., Biała K., Piekarz M., Flechsig G.-U.: Electrochem. Commun. *9*, 2346 (2007).
2. Wachholz F., Gimsa J., Duwensee H., Grabow H., Gründler P., Flechsig G.-U.: Electroanalysis *19*, 535 (2007).
3. Flechsig G.-U., Gimsa J., Gründler P., Grabow H.: Patent DE 10 2006 006 347 B3 (2006).
4. Lau C., Flechsig G.-U., Gründler P., Wang J.: Anal. Chim. Acta *554*, 74 (2005).
5. Duwensee H., Flechsig G.-U., Wang J.: in prep.

## OP72

## DEVELOPMENT OF AN ORDERED ARRAY OF MACROPOROUS MICROMETER OPTOELECTROCHEMICAL SENSORS

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An ordered array of macroporous optoelectrochemical sensors is presented; this device presents interesting peculiarities combining the electroanalytical properties of the macroporous electrode surface, and the optical characteristics of the coherent fiber bundle used as substrate. This novel array can find application as analytical tool, for example for electrochemiluminescence (ECL) imaging, but can even be used as new substrate for Surface-Enhanced Raman Scattering (SERS)[1,2]. The device was fabricated by chemical etching of a coherent optical fiber bundle to produce an array of microwells. The macroporous surface inside the micrometer pores was obtained by template synthesis using colloidal crystals. The artificial opal is created in each microwell by solvent evaporation of a latex beads suspension (Fig. 1). Two different methods were used to deposit gold within the self assembled beads. On one hand, we used an electroless deposition method[3], based on the activation of the polystyrene beads surface by deposition of silver nanoparticles, and on the other hand, an electrochemical deposition technique[4] was employed. As far as the latter method is concerned, a preliminary step is necessary to insulate the cladding between the optical fibers, to obtain the electrodeposition only inside the micropores. After removing the particles a macroporous surface is obtained inside the microwells usable for SERS application or electroanalytical analyses.

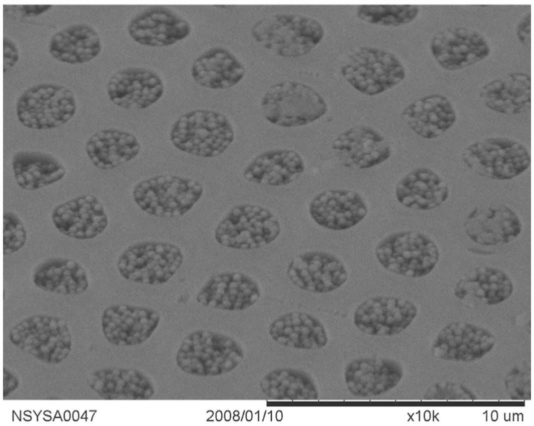

Fig. 1. **Ordered microwell array obtained in an etched optical fiber bundle, filled with latex beads**

REFERENCES

1. Bartlett P. N., Baumberg J. J., Coyle S., Abdelsalam M. E.: Faraday Discuss. *125*, 117 (2004).
2. Guieu V., Lagugné-Labarthet F., Servant L., Talaga D., Sojic N.: Small *4*, 96 (2008).
3. De Leo M., Pereira F. C., Moretto L. M., Scopece P., Ugo P.: Chem. Mater. *19*, 5955 (2007).
4. Szamocki R., Reculusa S., Ravaine S., Bartlett P.N., Kuhn A., Hempelmann R.: Angew. Chem. Int. Ed. Engl. *45*, 1317 (2006).

## OP73

## FULL-AUTOMATED ANALYSIS SYSTEM FOR ON FIELD CADMIUM SPECIATION

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Among the multitude of highly toxic pollutants, heavy metals have a special place, because they are considered as dangerous even at the low $\mu g\ L^{-1}$ level concentration.

Origins of environmental cadmium pollutions are varied but it usually comes from wastewaters or industrial effluents. Cadmium is used in battery and coating industries but it is also a by-product of lead, copper or zinc mineral extractions. This cadmium is mainly inorganic but its speciation can be modified by its close environment.

In order to have better representative analyses so better information about the contamination degree of the medium, measurements have to be carried out quickly after sampling. A lot of analytical techniques are employed to quantify heavy metals but only a few of them can be achieved on field.

Stripping voltammetry gives the ability to proceed to *in situ* and on field measurements[1,2]. Furthermore voltammetry inherently informs about thermodynamic and kinetic accessible fraction of heavy metals species which is comparable to the bioavailable fraction[3]. Moreover than on site measurements, this method gives information about cadmium speciation.

A full-automated analysis system is developed and is presented in this study. The central key of the apparatus is the electrochemical sensor which is connected to a potentiostat and an automat both piloted by a personal computer.

### The sensor

Hg-coated modified screen printed electrode previously used in our laboratory has been adapted to the constraints due to automatic measurements[4,5]. Various modifications of electrode screen printing process and mercury film deposition permit to obtain good sensor's reproducibility with a variation of sensitivity inferior to 10 % considering 11 different electrodes. In addition, the relative standard deviation of 2 % reached, considering 160 consecutive analyses, shows the excellent repeatability of measurements. Analyses were done using square wave anodic stripping voltammetry.

The limits of detection and quantification for a deposition time of 2 minutes and a total analysis time inferior to 5 minutes are respectively 0.15 and 0.50 μg($Cd^{2+}$) $L^{-1}$. These potentialities illustrate our sensor possibilities to the ultra-trace low-level applications.

**The automat**

Advantages of this kind of apparatus are twice. The first one is the automation of the entire analysis process previously carried out by the user, from the modification of the sensor to the results data processing. The device is composed of several containers connected to several electrochemical cells which are automatically filled or emptied with the needed solutions. It permits then to neglect analyses irreproducibility due to the manipulator. The second advantage is the adaptability of the automat to any type of sensor since the connection of the electrode is possible and the concerned analytical technique is managed by the potentiostat.

This device can then be used as an on field cadmium speciation analyses system. Moreover than cadmium detection, the electroactivity range of our electrode and the adaptability of the automat allow an enlargement of applications to lead, zinc, copper or arsenic. This device can also be considered as a powerful sensor-development tool. Indeed, it is possible to proceed for example to immunoanalyses or to the development of immunosensors only by modifying the containers content and the electrochemical process *via* the potentiostat.

**Applications to real samples**

Primary applications to real sample which will be presented are promising. For example, the following figure illustrates an application to a river water contaminated with cadmium.

Comparison between ICP-MS results, 0.73±0.03 μg ($Cd^{2+}$) $L^{-1}$ and electrochemical results, 0.70±0.08 μg($Cd^{2+}$) $L^{-1}$ indicates the potentialities of our sensor and allows to say that all the dissolved cadmium is present in its bioavailable and toxic forms.

Coupled with an organic matter destruction module, this device will be able to provide information not only about the bioavailable fraction but also about the total quantity of heavy metals present in solution.

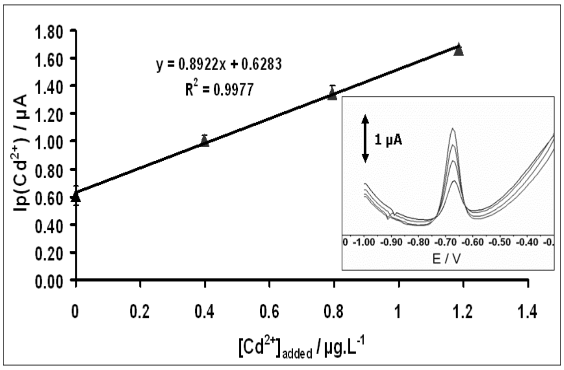

Fig. 1. **Measurement of the cadmium present in a river water by standard additions of cadmium**

REFERENCES

1. Buffle J., Tercier-Waeber M.-L.: Trends Anal. Chem. *24*, 172 (2005).
2. Baldo A., Daniele S., Ciani I., Bragato C., Wang J.: Electroanalysis *16*, 360 (2004).
3. Sigg L., Black F., Buffle J., Cao J., Cleven R., Davison W., Galceran J., Gunkel P., Kalis E., Kistler D., Martin M., Noel S., Nur Y., Odzak N., Puy J., van Riemsdijk W., Temminghoff E., Tercier-Waeber M.-L., Toepperwien S., Town R. M., Unsworth E., Warnken K. W., Weng L., Xue H., Zhang H.: Environ. Sci. Technol. *40*, 1934 (2006).
4. Betelu S., Parat C., Petrucciani N., Castetbon A., Authier L., Potin-Gautier M.: Electroanalysis *19*, 399 (2007).
5. Parat C., Authier L., Betelu S., Petrucciani N., Potin-Gautier M.: Electroanalysis *19*, 403 (2007).

## OP74

## ELECTROCHEMICAL SCANNING TUNNELING MICROSCOPY ON SELF-ASSEMBLY MONOLAYER ON Au(III)

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The ordered monolayer structures of molecules at solution/electrode interface have been studied extensively as their importance both in fundamental researches and technological applications[1–3]. Of particular interesting are their interactions with the substrates and between themselves, which are essential for understanding their physical and chemical as well as their potential dependence properties and optimized applications. The nature of the bonding between the molecule and the support, as reflected in the electronic charge distribution and the geometric configuration of the molecule-support entity, in principle, can be addressed by obtaining submolecular resolution electrochemical scanning tunneling microscopy (ESTM) images of molecules adsorbed on the interested substrate by self-assembling.

Au(III), one of the facets appeared on a gold bead surface, is prepared following the Clavilier's method[4] and used as the substrate for sample preparation. The ESTM measurement was performed with a Nanoscope E instrument equipped with a bipotentiostat (DI, Santa Barbara, CA). All STM images were recorded in the constant-current mode. Two clean Pt wires were used as a quasi-reference electrode and a counter electrode (CE) in the STM experiments. The freshly etched tungsten tip was coated with nail polish and solidified at least 15min (the leakage current of tip < 10 pA).

Three kinds of molecules, metal (II) phthalocyanines (MPc) as well as their derivatives, DNA bases and 6-mercapto--1-hexanol (MHO) were studied by ESTM on Au(III) electrode. (*1*) The geometric configurations of MPc (Ni and Cu) were reflected as the four-leaf pattern shape with dark hole in the center which depends on the *d* orbital of the central metal (II) near the Fermi energy. The ordering of MPc adlayer is affected by the side chains of MPc molecules. (*2*) Two dimen-

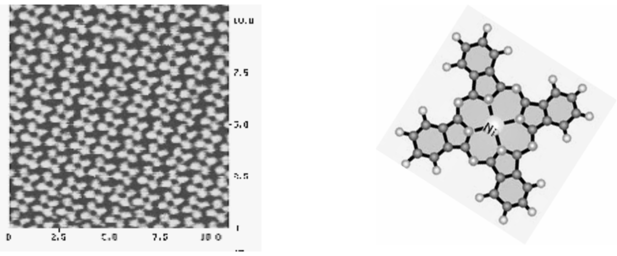

Fig. 1. **ESTM image of NiPc/Au(III)** (*left*) **and the planar molecular model of NiPc** (*right*)

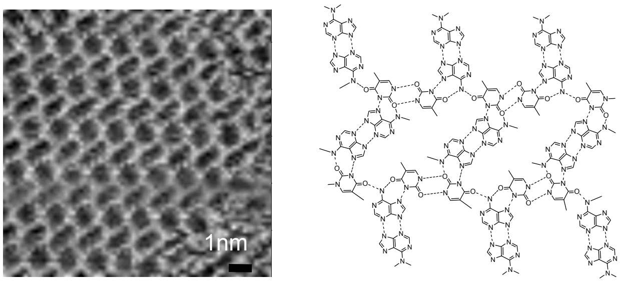

Fig. 2. **ESTM image of mixtured adenine and thymine/Au(III)** (*left*) **and the proposed network structure** (*right*)

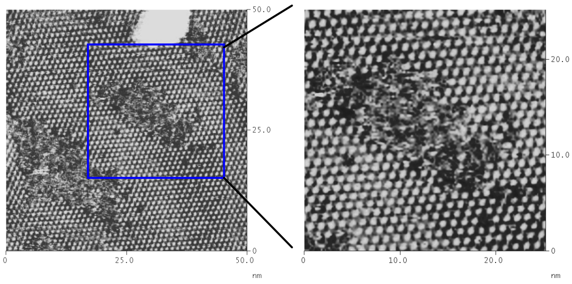

Fig. 3. **ESTM images of the initial stage of MHO adsorption on coronene/Au(III)**

sional phase transition of DNA bases adenine and thymine as well as their mixture were investigated by electrochemistry and STM. Two dimensional phase transitions and intermolecular interactions of DNA bases adenine and thymine were studied in details. The net work structure of adenine and thymine are observed. (*3*) The monolayer of coronene on Au (III)could be replaced with MHO as revealed by electrochemical STM. The preformed coronene monolayer confined the reaction rate of MHO with Au. The replacement occurred initially at the elbow position on the reconstructed Au(III) and expanded from disorder to order and accompanied with the appearance of pits.

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REFERENCES

1. Yoshimoto S., Tada A., Suto K., Yau S.-L., Itaya K.: Langmuir *20*, 3159 (2004)
2. Tao N., Rose J., Lindsay S.: J. Phys. Chem. *97*, 910 (1993).
3. Zhang J., Chi Q., Ulstrup J.: Langmuir *22*, 6203 (2006).
4. Clavilier J., Faure R., Guinet G., Durand R.: J. Electroanal. Chem. *107*, 205 (1980).

## OP75

## COMPARISON OF CARBON PASTE ELECTRODES PREPARED USING RTILS AS A BINDER

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Room temperature ionic liquids (RTILs), ionic salts with melting temperature under 100 °C, are now a frontier area of research. Their interesting properties, eg. chemical and thermal stability, conductivity, solubility of organic and inorganic compounds as well as plentiful modification possibilities offer utilization in many areas, including electrochemistry[1].

Recently, a new kind of carbon paste electrodes, using RTILs as a binder (IL-CPE), was introduced[2]. Original reason for the preparation of IL-CPE was seeking after the paste binder with charge transfer rate high enough for electrocatalytic modificators incorporation, but soon more interesting features of IL-CPE were discovered. Easier accesibility of the paste surface caused by lower hydrofobicity led to enhanced reversibility of electrochemical reaction[3–5]. Accummulation of ionic compounds was also enabled, which was not possible at non-polar binder[5]. However, large capacitive charging currents result in a very high background current in comparison with traditional carbon paste electrodes[2,4,5].

Various compositions of IL-CPE were tested, including partial replacement of non-polar paste binder[6] or different kinds of RTILs (ref.[5]). The results obtained show us the possible adjustable electrode properties.

The aim of the study is to compare the electrochemical behaviour of IL-CPEs prepared of variety of RTILs and in comparison to traditional paste electrode.

*Financial support of Ministry of Education, Youth and Sports of the Czech Republic (projects LC 06035 and MSM 0021620857) is gratefully acknowledged.*

REFERENCES

1. *Electrochemical Aspects of Ionic Liquids* (Ohno H., ed.) . John Wiley, New York 2005.
2. Liu H., He P.: Electrochem. Commun. *7*, 1357 (2005).
3. Sun W., Yang M.: Electroanalysis *19*, 1597 (2007).
4. Zheng J., Zhang Y.: Talanta *73*, 920 (2007).

5. Maleki N., Safavi A.: Anal. Chem. *78*, 3820 (2006).
6. Wang S. F., Xiong H. Y.: Electrochem. Commun. *9*, 807 (2007).

## OP76
## VOLTAMMETRY OF ANTIOXIDANTS ON CARBON ELECTRODES MODIFIED BY MULTI-WALLED CARBON NANOTUBES

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Antioxidants (AO) are one of the main objects of analysis and investigations in life sciences. Development of new techniques for the AO determination is very important. Voltammetry is characterized by simplicity, sensitivity, cost-efficiency, precision and speed and may be useful in AO analysis. Carbon nanotubes (CNT), as a novel form of carbon, have shown many interesting properties such as fast electron transfer rate and high electrocatalytic activity that permits to use CNT for the sensors creating in electroanalysis.

Voltammetric characteristics for oxidation of the most important S-containing and liposoluble AO on the stationary GC, CE and MWNT-GC, MWNT-CE electrodes are presented in table. 0.1 M $H_2SO_4$ and 0.1 M $HClO_4$ in acetonitrile have been chosen as supporting electrolytes for determination of S-containing and liposoluble AO, respectively. Schemes of analytes oxidation have been proposed.

Application of MWNT-modified electrodes leads to decrease of overpotential and increase of oxidation currents for the AO under investigation in comparison with unmodified electrode. Number of S-containing AO shows an electrochemical activity in available range of anodic potential on contrary to bare electrodes. Decrease of the low determination limit and enlargement the analytical range for AO determination have been obtained using electrodes nanoctructured by MWNT. Simple, expressive procedures for the voltammetric determination of the AO (methionine, unithiol, lipoic acid, α-tocopherol and retinol) in pharmaceuticals have been developed. The RSD of determination is not exceed 5 %. The method proposed is characterized by good reproducibility, speed and can be recommended for the pharmaceuticals quality control.

Table
Voltammetric characteristics of AO oxidation

| Compound | Electrode | Oxidation potential [V] | $I_{mod}/I$ |
|---|---|---|---|
| Cysteine | GC | +0.80 | – |
| | MWNT-GC | +0.60 | 5 |
| Glutathione | GC | – | – |
| | MWNT-GC | +0.65 | – |
| Methionine | GC | – | – |
| | MWNT-GC | +1.15 | – |
| Unithiol | GC | – | – |
| | MWNT-GC | +0.60 | – |
| Lipoic acid | GC | +0.91 | – |
| | MWNT-GC | +0.81 | 1.6 |
| α-Tocopherol | CE | +0.72, 1.01 | – |
| | MWNT-CE | +0.51, 0.85 | 1.8 |
| Retinol | CE | +0.87, 1.11 | – |
| | MWNT-CE | +0.80, 1.04 | 2.0 |

## OP77
## HISTORY OF THE BEGINNING OF THE J. HEYROVSKY INSTITUTE

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At the early months of 1950 Professors J. Heyrovský and R. Brdička carried out research in polarography at the Department of Physical Chemistry of the Charles University in Prague, at Albertov. In the preparation of formation of the Czechoslovak Academy of Sciences, it was decided to inaugurate six, so called Central, research institutes, separate from the University. One of them was Central Polarographic Institute to be headed by Professor J. Heyrovský, located at Opletalova 25 in Prague 2, close to the Wenceslaus Square. In the Summer of 1950 Prof. Heyrovský was joined there by six students in the finishing phase of their theses, namely J. Vogel, J. Říha, A. Vlček, J. Mašek, M. Březina and myself. Soon they were joined there with Dr. J. A. V. Novák as Vice-Director, by J. Kůta, I. Smoler, P. Valenta, L. Šerák, J. Peizker, J. Volke, V. Volkeová and R. Kalvoda and later by J. Koryta. With the official fundation of the Czechoslovak Academy of Sciences in 1952, the institute was renamed to Polarographic Institute of the Czechoslovak Academy of Sciences. All research in the Institute was involved in the development of fundamental and practical applications of polarography. With the growth of the Institute, a separate location was found at Vlašská 9 on Malá Strana and later a separate laboratory dealing with fuel cells at Hostivař. Professor R. Brdička remained for some time at the Charles University and became the Director of the Institute of Physical Chemistry of the Czechoslovak Academy of Sciences. Eventually, the two Institutes were merged into J. Heyrovsky Institute of Physical Chemistry and Electrochemistry, which still later became the J. Heyrovsky Institute of Physical Chemistry.

## OP78

## WHAT DO WE KNOW ABOUT DETERMINATION OF AMINO ACIDS?

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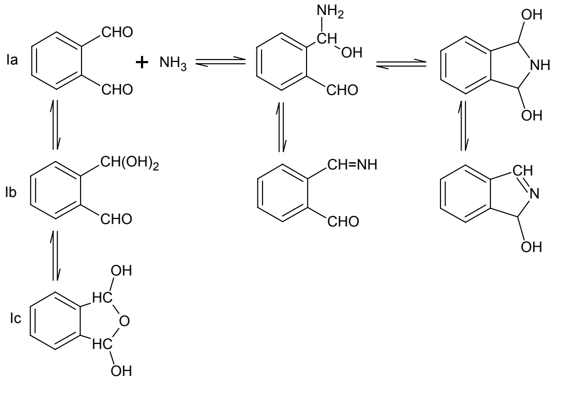
The reaction with ninhydrin proved to be insufficiently sensitive for the determination of amino acids. Roth[1] in 1971 suggested replacement of ninhydrin by orthophthalaldehyde (OPA). He observed that a florescent species is formed. The intensity of florescence was increased, when borohydride or thiolate ions were added. He first assumed that these added anions act as reducing agents, but later was found that they react in nucleophilic additions. Roth also observed that the intensity of florescence was higher when the strong nucleophile was added before the amino acid then when the sequence was reversed. The florescent species was identified as an isoindole derivative[2], which can undergo consecutive reactions.

Mechanisms of the formation of the fluorescent species were unknown. Attempts to elucidate this mechanism based solely on product identification were unsuccessful, as the solution chemistry of OPA was not considered and improbable steps, like fast reversible cleavage of C-H band, assumed[2]. In this situation, analytical methods based on reaction of OPA with amino acids in the presence of $RS^-$ or $CN^-$ ions were developed empirically. The reaction conditions reported in more than 700 papers differed considerably[2]. The reaction was also used in commercial instruments for determination of amino acids.

We have shown[3] that in aqueous solutions OPA exists in three different forms in equilibrium – the unhydrated form Ia (18 %), monohydrated acyclic form Ib (7 %) and cyclic hemiacetal form Ic (78 %). These forms are in equilibria, the rate of establishment of which is acid and base catalyzed.

In the next step we followed reactions of OPA and $NH_3$ and 2-aminoethanol (colamine). The first was chosen as the simplest amine, the second because it has $pK_a$ 9.5, close to that of e.g. glycine (9.3), but the reaction form of which does not contain the carboxylate group, that can further complicate studied reactions. With both amines a hetrocyclic species is formed that is reduced at about −1.6 V. Following reduction waves of OPA at −0.9 V and −1.2 V it was shown that OPA is in equilibrium with the hetrocyclic species. The rate of establishment of this equilibrium is acid catalyzed. For the reactions with 2-aminoethanol the establishment of this equilibrium is fast. For the reaction with $NH_3$ it was possible to show that the carbinolamine formed in the addition yields an imine in a side reaction. The driving force of the reaction is nevertheless the ring formation. So the imine is rapidly formed back to colamine which undergoes the ring formation (Scheme 1).

Reactions of OPA with glycine and its ester are currently investigated.



Scheme 1. **Reaction of OPA and ammonia**

REFERENCES

1. Roth M.: Anal. Chem. *43*, 880 (1971).
2. Zuman P.: Chem. Revs. *104*, 3213 (2004) and references therein.
3. Salem N., Andreescu S., Kulla E., Zuman P.: J. Phys. Chem., A *111*, 4658 (2007).

# POSTER PRESENTATIONS

## PP001

## LACTATE DEHYDROGENASE BIOSENSOR BASED ON AN HYBRID CNT-CONDUCTING POLYMER ELECTRODE

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Biosensors based on nanostructured electrochemical transducers have a great interest because of their particular advantages. Carbon nanotubes (CNTs) and conducting polymers have been used successfully for the preparation of hybrid electrodes which exhibit special properties due to the synergic effect from both components. However, poly(3--methylthiophene) P3MT has been scarcely applied for the fabrication of composite materials. In a previous report, we synthesized a P3MT/ CNTs hybrid composite onto a glassy carbon electrode (GCE)[1]. Recent investigations in our lab have revealed that this type of hybrid electrodes possess the ability to decrease significantly, the overpotential for electrochemical oxidation of $H_2O_2$ and NADH.

In this communication, a lactate biosensor in which the enzyme lactate dehydrogenase (LDH) was immobilized onto a CNTs-P3MT-GCE has been developed. The resulting design is very attractive because of its simplicity, high sensitivity and low potential without using redox mediators.

The influence of experimental variables that could affect the performance of the biosensor: enzyme immobilization procedure, CNTs loading, applied potential, pH and $NAD^+$ concentration, were investigated in order to optimize the electroanalytical characteristics of the amperometric detection.

A good electroanalytical behaviour of the hybrid electrode was observed. The NADH analytical signal obtained by CV in 0.1 M PBS at pH 7.4 was approximately, three times higher at CNTs-P3MT-GCE than those at CNTs-GCE or P3MT-GCE. Furthermore, amperometric measurements at the LDH biosensor in stirred 0.1 M PBS pH 8.0 in the presence of 2.5 mM $NAD^+$, using 300 mV as the potential value, allowed the achievement of a quantification limit of 1 μM lactate. A good electrode-to-electrode reproducibility (RSD: 7.4 %, n=5) was also obtained. The influence of other species: ethanol, citric, malic, tartaric, uric (UA) and ascorbic (AA) acids was also investigated. Only UA and AA interferred, but this effect can be drastically reduced by casting a Nafion film over the working electrode.

REFERENCE

1. Agüí L., Peña-Farfal C., Yáñez-Sedeño P., Pingarrón J. M.: Electrochim. Acta *52*, 7946 (2007).

## PP002

## STUDY OF METAL COMPLEXATION BY THIOL-RICH PEPTIDES USING BISMUTH FILM ELECTRODES

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Living beings have developed different strategies to face up toxicity of heavy metals. Particularly, plants response with immobilisation, exclusion, chelation and compartmentalisation of the metal ions, cleaning up and restoring the damage ecosystems, main objective of the phytoremediation technologies.

A number of metal-binding ligands have nowadays been recognised in plants. Among them, phytochelatins (PC) play a key role since they are capable to bind metal ions -mainly via thiolate coordination-, to complex and then to place them into vacuoles where they are no longer toxic. PC's are polypeptides synthesized enzymatically by plants and constituted basically by three amino acids (Glu, Cys and Gly) with the general structure $(\gamma\text{-Glu-Cys})_n\text{-Gly}$, where *n* can be as high as 11, but it usually ranges from 2 to 6.

To understand the role of phytochelatins in the detoxification of metals, mechanisms of formation of PC-metal complexes must be examined. The combined use of voltammetric techniques and Multivariate Curve Resolution by Alternating Least Squares (MCR-ALS) has proved to be useful to obtain the possible stoichiometries and some suggestions about the relative stability of the complexes, especially with Cd(II) and Zn(II). However, for the study of Pb(II)-PC systems this approach presents the problem that thiol-rich peptides facilitate the oxidation of mercury electrodes, producing many anodic signals (of free ligands and some complexes) which appear in the reduction region of Pb(II)[1]. These anodic signals strongly overlap with the electrodic signals to be studied and, moreover, they undergo potential shifts and over-distort baselines, complicating in all cases a complete resolution of the complexation mechanisms.

A suitable solution could be the use of electrodes based in other material than mercury, expecting the non-formation of these signals and therefore the simplification of electroanalytical data. Bismuth film electrode (BiFE)[2] is an electrochemically attractive and environmentally friendly electrode that has proved to be a good alternative to the prevalent use of mercury electrodes for the determination of trace metals and organic compounds[3].

The present work tries to examine the possibilities of the BiFE for the study of the complexation of phytochelatins and related compounds by lead, checking what species of the complexation process provide signals in this electrode, its dependence on metal speciation, and the possible application of MCR-ALS.

As regards to the latest point, the applicability of this chemometric tool needs a good linearity of the data, but a peak splitting effect has been observed for some heavy metals in stripping techniques using bismuth film electrode[4]. Thus, a rief study of this possible behavior in differential pulse voltammetry, the more widespread technique used in complexation analysis, is carried out.

*The authors acknowledge support of the Spanish Ministry of Education and Science (Project CTQ2006-14385-C02-01/ BQU) and from the Generalitat of Catalonia (project 2005SGR00186).*

REFERENCES

1. Alberich A., Ariño C. Díaz-Cruz J. M., Esteban M.: Talanta *71*, 344 (2007).
2. Wang J., Lu J., Hocevar S. B, Farias A. M., Ogorevc B.: Anal. Chem. *72*, 3218 (2000).
3. Economou A.: Trends Anal. Chem. *24*, 334 (2005).
4. Serrano N., Alberich A., Díaz-Cruz J. M., Ariño C., Esteban M.: Electrochim. Acta, submitted.

## PP003

## CYP250 2B4 COVALENTLY BOUNDED TO CARBON AND GOLD SCREEN PRINTED ELECTRODES BY DIAZONIUM AND THIOLS MONOLAYERS

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Modification of carbon and gold screen printed electrodes (SPEs) surfaces has been performed in order to ensure the covalent immobilization of biological molecules. SPE units based on three-electrode configurations have been homemade printed by using a DEK 248 (Fig. 1). Carbon counter, Ag/AgCl reference and gold or carbon working electrodes have been used.

Fig. 1. **Screen printed carbon electrodes units developed**

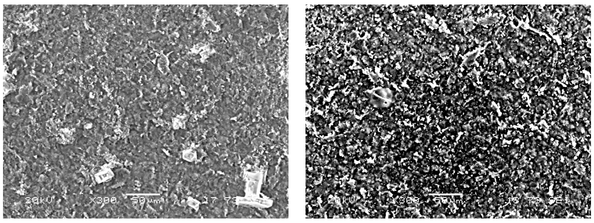

Fig. 2. **Carbon working electrode modified by gold nanoparticles (left) and by gold nanoparticles-MPA (right)**

A first step consisted of the electrochemical reduction of diazonium salts onto the carbon SPEs, which leads to covalent attachment of aryl radicals. This chemical modification of the composite may improve its properties[1–4].

In the case of gold SPEs, 3-Mercaptopropionic acid (MPA) was self assembled[5]. The performance of this working electrode in the building of biosensors has been improved by electrochemical deposition of gold nanoparticles before the self-assembled monolayer (SAM) modification.

The latter modification has also been attempted onto the carbon working electrodes (Fig. 2, ref.[6]), showing an improvement of conductivity defined by the analysis of the cyclic voltammetric peaks of ferricyanide system.

Then, these four different modified SPEs have been covalently bonded to Cytochrome P450 2B4 (CYP450) for the selective determination of Phenobarbital.

Experimental variables in the enzyme immobilization and in the chronoamperometric determination of PB have been optimized by means of the experimental design methodology.

Reproducibility, repeatability and limit of detection of the CYP450 biosensor have been analyzed. In order to check the performance of the proposed methods, the sensors have been applied to the PB determination in commercial pharmaceutical drugs.

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REFERENCES

1. Allongue P., Delamar M., Desbat B., Fagebaume O., Hitmi R., Pinson J., Saveant J. M.: J. Am. Chem. Soc. *119*, 201 (1997).
2. Pinson J., Podvorica F.: Chem. Soc. Rev. *34*, 429 (2005).
3. Corgier B. P., Marquette C. A., Blum L. J.: J. Am. Chem. Soc. *127*, 18328 (2005).
4. Alonso-Lomillo M. A., Rudiger O., Maroto-Valiente A., Velez M., Rodriguez-Ramos I., Munoz F. J., Fernandez V. M., De Lacey A. L.: Nano Lett. *7*, 1603 (2007).
5. Susmel S., Guilbault G. G., O'Sullivan C. K.: Biosens. Bioelectron. *18*, 881 (2003).
6. Renedo O. D., Martinez M. J. A.: Anal. Chim. Acta *589*, 255 (2007).

## PP004

## VOLTAMMETRIC LEAD DETECTION USING LTCC BASED MICROFLOW SYSTEM

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Electrochemical detectors are an attractive alternative in microfluidics because small sample volumes are needed and provide low detection limits.

The aim of the present work is the construction of miniaturized voltammetric system for the determination of heavy metals., in this case lead ion. The microanalytical system was constructed using the LTCC (Low Temperature Co-Fired Ceramics) technology. Monolithic integration of fluidic and detection system was done using the same technology and substrate. The voltammetric system includes two platinum sheets (5 × 5 mm) acting as working and counter electrode and a miniaturized Ag/AgCl reference electrode fabricated using embebed Ag conductive pads screen-printed over the auxiliary microfluidic channel. The dimensions of the whole microsystem was 55 × 25 × 2 mm (see Fig. 1).

Results obtained demonstrate the posibility to determine lead ions. However, the detection limit obtained was high for its aplication in drinking water. Moreover, the device has a limited life time due to a irreversible passivation of working electrode under the working conditions. Better results had been obtained in preliminary experiments when platinium was replaced for gold microchip as working electrode.

In order to improve the analytical features and increase the device life span, the performance of other metals like gold and silver as working electrodes will be tested.

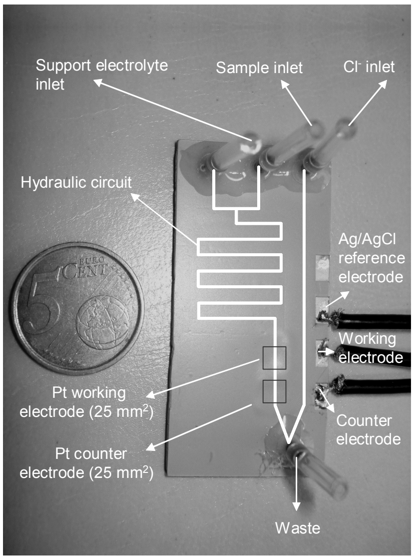

Fig. 1. **LTCC device picture**

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## PP005

## DETERMINATION OF As(III) USING SILVER NANOPARTICLE-MODIFIED SCREEN-PRINTED ELECTRODES

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Arsenic is one of the most toxic elements found in nature, and it constitutes one of the main concerns in relation to human health. Arsenic is second only to lead as the main inorganic contaminant in the original US Environmental Protection Agency's (EPA) National Priority List (NPL) of Superfund sites. Arsenic can be found in drinking water, in the air as volatile arsines, and in soil, where it can concentrate if absorbed on soil components. Consumption of water with high concentrations of this non metal over an extended period of time causes serious diseases, including development of cardiovascular and peripheral vascular disease anomalies, neurological and neurobehavioral disorders, diabetes, hearing loss, portal fibrosis of the liver, lung fibrosis, hematological disorders, and carcinoma, especially in rural and semi-urban areas where water irrigates food or drinking water is often used without treatment[1].

Several analytical techniques have been used for arsenic determination at trace levels, such as atomic absorption spectrometry[2], atomic fluorescence spectrometry[3], and high-performance liquid chromatograph-inductively coupled plasma mass spectrometry (HPLC-ICPMS)[4]. The most reliable techniques are more suitable for laboratory conditions only and are, in addition, time consuming. In contrast, electrochemical methods provide accurate measurements of low concentrations of metal ions at the ppb levels with rapid analysis times and low cost instrumentation.

Screen-printed electrodes are planar devices with plastic substrates that are coated with layers of electroconductive and insulating inks at a controlled thickness. The advent of screen-printed (thick-film) technology has made it possible to mass-produce inexpensive disposable electrodes for use with electrochemical instruments[5].

The design of new nanoscale materials has acquired ever-greater importance in recent years due to their wide-ranging applications in various fields. Among these materials, metallic nanoparticles are of great interest due to their important properties and their numerous possible applications. Moreover, the advent of screen-printed (thick-film) technology has made it possible to mass-produce inexpensive disposable electrodes for use with electrochemical instruments.

The aim of this work is to determine As(III) by differential pulse voltammetry (DPV) using screen-printed electrodes modified with silver nanoparticles and, to the best of the author's knowledge, presents the first ever electrochemical detection of As(III) with this type of electrodes.

*The financial support made available by the Junta de Castilla y León (BU022A07) and the Ministerio de Educación y Ciencia (MAT2005-01767) is gratefully acknowledged.*

REFERENCES
1. Mandal B.K., Suzuki K.T.: Talanta *58*, 201 (2002).
2. Niedzielski P.: Anal. Chim. Acta *551*, 199 (2005).
3. Ma G., Xie W. B., Liu J., Li X. Y., Jin Y. W.: Spectrosc. Spectr. Anal. *27*, 807 (2007).
4. Brennan R. G., Murdock S. A. E. O., Farmand M., Kahen K., Samii S., Gray J. M., Montaser A.: J. Anal. At. Spectrom. *22*, 1199 (2007).
5. Wang J., Lu J., Tian B., Yarnitzky C.: J. Electroanal. Chem. *361*, 77 (1993).

## PP006

## ANALYSIS OF MACROCYCLIC LACTONE MYCOTOXINS IN MAIZE FLOUR SAMPLES BY CAPILLARY ELECTROPHORESIS WITH AMPEROMETRIC DETECTION

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Mycotoxins are secondary metabolites produced by fungal species, growing on agricultural products during cultivation, harvest, transport and storage. Their occurrence in food has been recognized as potential human hazard either caused direct contamination of grains and fruits and their products or by "carry over" of mycotoxins and their metabolites in animal tissues. Zearalenone (ZON) and its metabolites α-zearalenol (α-ZOL) and β-zearalenol (β-ZOL) are produced by *Fusarium* species, which colonize several grains and high amounts of ZON can most frequently be found on maize, wheat, oats and barley. Maximum levels of 200 and 100 ppb have been fixed for ZON in unprocessed corn and unprocessed cereals other than corn, respectively.

In this communication we report on a new analytical scheme for the screening and quantification of ZON, α-ZOL and β-ZOL by capillary electrophoresis with amperometric detection in extracts collected by supercritical fluid extraction (SFE) from maize flour samples. The sample screening was carried out by capillary zone electrophoresis (CZE) using 25 mM borate running buffer at pH 9.2 and 25 kV as separation voltage and following the amperometric signal at +700 mV of a carbon paste electrode (CPE, 0.5 mm diameter). In this way, total mycotoxins containing is determined and samples could be processed in 4 minutes with a detection limit of 20 ppb, enough to discriminate between positive (more than 200 ppb total mycotoxins, reference value stablished for ZON by directive 2005/38/EC)) and negative samples (less than 200 ppb total mycotoxins). Positive samples were then subjected to CZE separation and quantification of each analyte with 50 mM borate running buffer modified with 30% methanol at pH 9.7 and 17.5 kV as separation voltage. Under these conditions, separation is achieved in 15 minutes with detection limits of 50 ppb for each analyte.

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## PP007

## MELDOLA'S BLUE/SINGLE-WALLED CARBON NANOTUBES/SOL-GEL COMPOSITE ELECTRODE FOR ELECTROCHEMICAL ANALYSIS OF NADH

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An electrochemical sensitive electrode for NADH determination was developed based on the integration of the redox mediator (Meldola's blue, MB) and single-walled carbon nanotubes (SWNT) with polymeric matrix (silica sol-gel). The resulting composite material was used for coating the surface of screen-printed electrodes and investigated and characterized by electrochemical methods. Analytical parameters of the sensors with and without SWNT in the hybrid film were compared, and the results showed that analytical performance of the sensor could be improved greatly after introduction of the SWNT (sensitivity 3 times higher and a wider linear range). Experimental parameters of the NADH sensor, such as applied potential, amount of SWNT, drying time for sol-gel matrix were studied and optimized. The applied working potential (–0.050 V vs. Ag/AgCl) is low, consequently avoiding the interference from electroactive compounds and thus increasing the selectivity of the sensor.

This nanomaterials-based composite may be used as electrochemical transducers and have potential application for designing a variety of NAD+-dependent electrochemical biosensors.

*We acknowledge financial support from MECT contract no. 1637/2007, 51-006/2007, 11-055/2007 and Bioprof.*

REFERENCES
1. Song Z., Huang J.-D., Wu B.-Y., Shi H.-B., Anzai J.-I., Chen Q.: Sens. Actuators, B *115*, 626 (2006).
2. Salimi A., Compton R. G., Hallaj R. : Anal. Biochem. *333*, 49 (2004).
3. Du P., Liu S., Wu P., Cai C. : Electrochim. Acta *53*, 1811 (2007).
4. Sampath S., Lev O.: J. Electroanal. Chem. *446*, 57 (1998).

## PP008

## ELECTROCHEMICAL ANALYSIS OF CORROSION BEHAVIOUR OF DENTAL AMALGAMS

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Dental Amalgam represents restorative material that has been used in dentistry since it's beginings. Throughout history of its use there have been certain dilemmas within dental profession that are focused on dental amalgam safety, regarding harmfulness of mercury from amalgam. Attitudes in this scientific area were, and still are, so divided, that we speak about three "amalgam wars". Mercury is one of basic components of dental amalgam. From toxicological point of view it is one of the most toxic heavy metals, considering all possible risks, both for dentists and patients. Antiamalgamists based their based their opposing on dental amalgam use mostly on the fact that there is a corrosion of amalgam within oral cavity, under different physical and chemical influences. Contrary, proamalgamists state that there is no proof that could support attitude that mercury from dental amalgam makes influence on general health and well-being of patient.

According to that, goals of this investigation were:

1. To examine quantity of corrosion of 5 different dental amalgams *in vitro,*
2. To make quantitative and qualitative analysis of corrosion products of analyzed amalgams *in vitro*,
3. To establish influence of polishing of dental amalgams on degree of their corrosion.

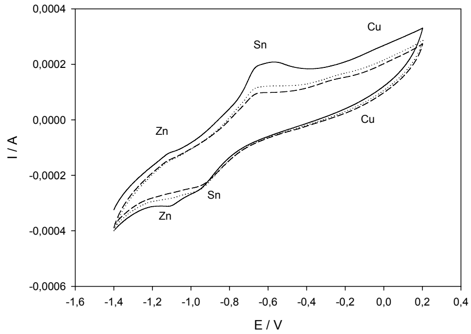

Fig. 1. **"NG70 Septalloy"in artificial saliva** (Quezada Duffo – Castillo), unpolished

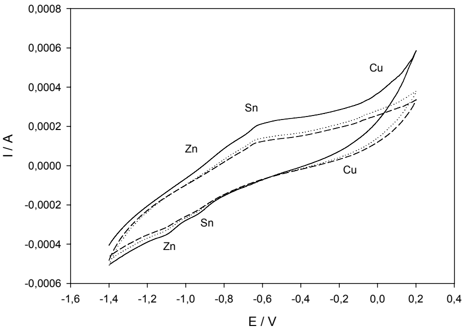

Fig. 2. **"NG70 Septalloy"in artificial saliva** (Quezada Duffo – Castillo), polished

Experimental material is represented by 5 different dental amalgams. Electrodes were made from them, respecting manner that is usual for electrochemical investigations. Those electrodes represented artificial teeth. Electrodes were tested using cyclic voltammetry (unpolished and polished) and inductively coupled plasma-mass spectrometry (ICP-MS) – polished. Electrochemical behavior of electrodes was tested in artificial saliva (Quezada Duffo – Castillo).

Cyclic voltammetry proved that corrosion of dental amalgams within defined potential range always happens. Its intensity depends on polishing of amalgam surface. They were determined as isotopes. According to this *in vitro* investigation, quantities of liberated mercury and other metals can not be consider harmful for patient, according to standards of World Health Organization (WHO). Polishing of dental amalgams has positive influence on their corrosion behavior because of reduced corrosion surface.

*The authors wish to acknowledge support for this work by the Ministry of education and science Sarajevo Canton and Federal ministry of education and science.*

REFERENCES

1. Wang J.: *Study of Electrode Reactions*. In: (Wang J., ed.). *Analytical electrochemistry*, 2nd ed., p. 28–59. Wiley-VCH, New York 2001.
2. Horasawa N., Nakajima H. J. L., Takahaschi S., Okabe T.: Dent. Mater *12*, 154 (1996).
3. Leung V. W.-H., Darvell B. W.: J. Dent. *6*, 475 (1997).
4. Duffo G. S., Quezada Castillo E.: Corrosion *60*, 594 (2004).
5. Karov J., Hinberg I.: J. Oral. Rehab. *28*, 212 (2001).
6. Yap A.V. J., Ng B. L., Blackwood D. J.: J. Oral. Rehab. *31*, 595 (2004).

## PP009

## FABRICATION AND APPLICATIONS OF INJECTION-MOULDED POLYMERIC CELL-ON-A CHIP DEVICES WITH INTEGRATED CONDUCTING ELECTRODES FOR ELECTROANALYTICAL MEASUREMENTS

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The use of microfabrication technologies enables the mass fabrication of small, reproducible, low-cost, portable and disposable sensors[1]. In particular, the integration of electrochemical analysis techniques into microfluidic devices is an area of increasing interest[2,3]. Injection-moulding offers some advantages over alternative micro-fabrication approaches: in addition to providing planar structures (such as channels) quickly and at a reasonable cost, it enables the creation of three-dimensional structures and the incorporation of preformed elements (such as electrodes) into the plastic during the moulding process.

In this work, cell-on-a-chip devices for electrochemical analysis were injection-moulded from polymeric materials to form plastic micro-devices. The electrodes were moulded from polystyrene loaded with carbon-fibres (40 %) By using a mould insert and an injection over-moulding procedure, the polymer electrodes were integrated into the device substrate. The moulded electrodes can be used unmodified or can be pre-coated either with metal layers (such as Au, Ag or Bi by e-beam/thermal evaporation and eletroplating) or with Ag/Cl paste, thereby forming working, reference and counter electrodes as required.

Furthermore, the moulded electrodes were be incorporated into micro-flow-cells. The flow channels in these devices were produced in a clear grade of polystyrene. Ultrasonic welding was used to bond the substrate containing the electrode to the substrate containing the microchannel. Figure 1(i) illustrates the two parts forming a microfluidic device while Figure 1(ii) shows the assembled micro-flow-cell.

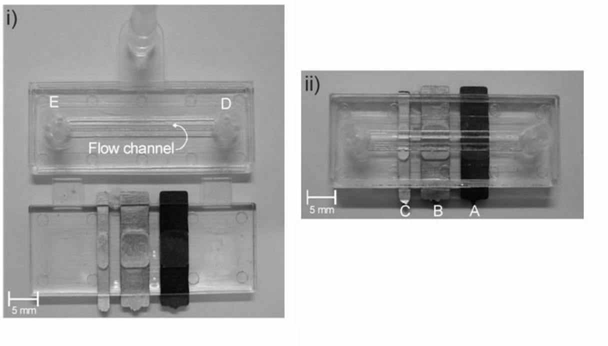

Fig. 1. **A example of an injection-moulded microfabricated device**: i) the two separate parts forming the flow cel, and; ii) the assembed flow-cell (A is the carbon CE, B is the gold WE, C is the Ag RE, D is the solution outlet and E is the solution inlet)

Electrochemical techniques such as cyclic voltammetry (CV), anodic stripping voltammetry (ASV), electrochemiluminescence (ECL) and catalytic adsorptive stripping voltammetry (CAdSV) have been tested on the micro-fabricated devices. In addition electrochemical procedures for *in situ* activation of the working electrodes, long term drift studies on the reference electrodes and device-to-device reproducibility were evaluated.

The results obtained demonstrate "proof-of-principle" of these cell-on-a-chip devices and suggest that they can be employed as disposable sensors in electronalysis.

REFERENCES

1. Becker H., Locascio L. E.: Talanta *56*, 267 (2002).
2. Suzuki H.: Electroanalysis *12*, 703 (2000).
3. Bakker E., Telting-Diaz M.: Anal. Chem. *74*, 2781 (2002).

## PP010

## UTILIZING OF BRDICKA REACTION FOR ANALYSIS OF LOW MOLECULAR MASS THIOLS

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Low molecular mass thiols represents group of compounds rich in –SH moieties. Due to reactivity of this moiety thiols play number of crucial roles in organisms e.g. control of gene expression and receptor signalling, signal transduction and heavy metal detoxification, and many others. Glutathione (GSH) belongs to the most important thiols. As a ubiquitous tripeptide thiol it is a vital intra- and extra-cellular protective antioxidant. Glutathione is found almost exclusively in its reduced form; since the enzyme, which reverts it from its oxidized form (GSSG) called glutathione reductase, is constitutively active and inducible upon oxidative stress. The sulfhydryl group of glutathione is highly reactive and is often found conjugated to other molecules such as nitric oxide (NO) via its sulfhydryl moiety. Particularly, nitrosation of the glutathione may serve as a signal event and/or as a deposition of NO to S nitrosoglutathione (GSNO). The aim of this work was to utilize Brdicka reaction to study GSH, GSSG and GSNO.

Primarily we optimized the experimental conditions to detect the thiols of interest. Under the optimal conditions we measured the dependence of Cat2 peak height on concentration of the thiols of interest. The dependence was linear from 5 to 100 $\mu g\ ml^{-1}$ for all thiols with $R^2$ higher than 0.99. The detection limits were lower than 1 $\mu g\ ml^{-1}$ for all thiols. Moreover the differential pulse voltammograms differed markedly according to thiols determined.

*We gratefully acknowledge the GACR 522/07/0692 for financial support to this work.*

REFERENCES

1. Vitecek J., Petrlova J., Petrek J., Adam V., Potesil D., Havel L., Mikelova R., Trnkova L., Kizek R.: Electrochim. Acta *51*, 5087 (2006).
2. Zitka O., Huska D., Krizkova S., Adam V., Chavis G. J., Trnkova L., Horna A., Hubalek J., Kizek R.: Sensors *7*, 1256 (2007).

## PP011

## STRATEGIES TO DEVELOP AMPEROMETRIC BIOELECTRODES FOR INFECTION DIAGNOSIS

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Most of infection diagnostic tests rely on detecting either the infecting agent (whole microorganism or selected molecules) or specific antibodies raised by the host[1]. We developed amperometric systems to detect both of these infection markers. In one approach, we detected antibodies to *Trypanosoma cruzi* parasite, by using a classical indirect immunoassay with electrochemical detection. We used recombinant proteins specifically designed to achieve three goals: *i*) to avoid cross-reactions with antibodies generated by the host during other diseases, *ii*) to link these molecules to the electrode in an oriented manner so as to enhance sensitivity and *iii*) to attach them covalently, so that the device could be reused after rigorous treatments. This strategy allowed us not only to efficiently and specifically detect the infection marker but also to regenerate the device to be reused in consecutive sample analysis, envisaging automatization[2]. The results obtained showed 100 % specificity for the entire positive and negative samples assayed. The sensitivity was in the same order as that obtained using a commercial ELISA kit following an indirect immunoassay format with spectrophotometric detection. The biosensors could be regenerated and then reused to analyze 10 different samples consecutively before showing a signal loss of 50 % ($P < 0.05$), with a cut-off value corresponding to a 20 % of the original signal measured. In another approach, to verify the presence of pathogenic bacteria, we detected by amperometry the consumption of catechol, a model substrate of bacterial enzymes. Considering that several bacteria have enzymatic systems that can degrade catechol, we enhanced the assay specificity by biologically releasing exclusively the enzymatic content of the target bacteria. Amperometries were performed in a classical three-electrode cell where a carbon paste electrode was the working electrode, using PBS as bathing electrolyte. The current difference obtained between the background and the tested sample was used to monitor the presence of catechol-degrading enzymatic system. Results obtained with samples of intact bacteria and specifically lysated showed significant differences ($P < 0.05$).

*ANPCyT & CONICET are acknowledged for grants PICTR2002-00057 and PIP5303, respectively.*

REFERENCES

1. Belluzo M. S., Ribone M. E., Lagier C. M.: Sensors *8*, 1366 (2008).
2. Lagier C. M., Marcipar I. S., Ribone M. E., Belluzo M. S., Camussone C. : INPI, Inscription N° P060103687.

## PP012

## SELECTIVE DETECTION OF MOLECULES WITH DIFFERENT SIZE BY GOLD ELECTRODE MODIFIED WITH DI-*n*-OCTADECYL-DISULPHIDE. APPLICATION TO VITAMIN $B_2$ DETERMINATION

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The objective of our work is modifying a gold electrode to allow selective arrival of molecules with different size at the surface of electrode through formed channels. It is got with the control of surface recover by di-*n*-octadecyl-disulphide. This control is obtained by change the concentra-

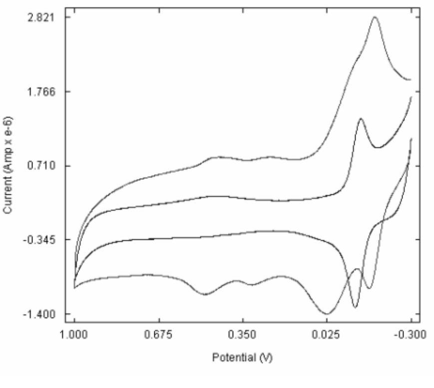

Fig. 1. **Cyclic voltammograms of vitamin $B_2$ in $H_2SO_4$ 0.1 M at 100 mV/s**. In red, without modification; in blue, with modification

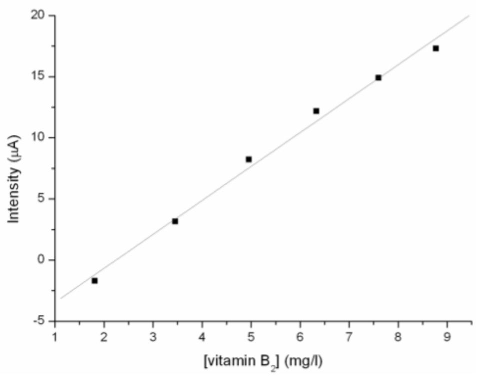

Fig 2. **Calibration curve of vitamin $B_2$ using SWV**.
I = 2,7748 C – 6,21106, $r^2$ = 0,996

tion of di-*n*-octadecyl-disulphide (solved in tetrahydrofuran) and stay time of the electrode in solution of the modifier. Ferrocen, hydroquinone and vitamin $B_2$ are the studied molecules. All work is being done in acid media (sulphuric 0,1 M) what is the most adequate media for its. The used electrochemistry technique is cyclic voltammetry what allows us to study oxidized and reduced molecules of ours compounds in the electrode surface. Each molecule and the mixture are studied with modifier and without modifier using different times and concentrations. In Fig. 1 is represented the response of the electrode with modifier and without modifier for vitamin $B_2$ and in Fig. 2 a calibration curve using the electrochemistry technique SWV. We are now working in the analysis of a drug formulation with vitamin $B_2$.We can deduce in these conditions if possible cause di-*n*-octadecyl-disulphide to make a physical barrier for molecules and to do selective detection by molecular size.

*We are grateful to MEC of Spain for financial support (CTQ2004-041/BQU).*

## PP013

## MINIATURE, MAINTENANCE AND INTERNAL SOLUTION FREE MULTI-ELECTRODE GALVANIC CELLS FOR POTENTIOMETRIC MEASUREMENTS

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Construction of the miniaturized, maintenance and internal solution free galvanic cells are an important challenge, because of the envisaged medical and biochemical applications. The use of conducting polymers in designing of such a cell was found to be especially beneficial.

It has been shown that electropolymerization is a convenient method to obtain conducting polymer films (CP films) doped with bulky dopants, e.g. metal complexing or biological buffer ligands, which retain their specific chemical properties inside CP-films[1–5]. In this way it is possible to obtain conducting polymer based reference or indicator membranes as well as mediating layers for solid-contact ion-selective or reference electrodes, consequently to obtain miniaturized, maintenance and internal solution-free multi-electrode galvanic cells. In this communication recent advances describing technology, electrochemical properties and selected applications are presented.

*Financial support from the State Committee for Scientific Research (KBN project 3T08E 085 30) is gratefully acknowledged.*

REFERENCES

1. Migdalski J., Błaż T., Lewenstam A.: Anal. Chim. Acta *322*, 141 (1996).
2. Migdalski J., Błaż T., Lewenstam A.: Chem. Anal. (Warsaw) *47*, 371 (2002).
3. Błaż T., Migdalski J., Lewenstam A.: Talanta *52*, 319 (2000).
4. Migdalski J., Błaż T., Żrałka B., Lewenstam A.: Anal. Chim. Acta *594*, 204 (2007).
5. Błaż T., Migdalski J., Lewenstam A.: Analyst *130*, 637 (2005).

## PP014

## THE SILVER AMALGAM FILM ELECTRODE IN ADSORPTIVE STRIPPING VOLTAMMETRIC DETERMINATION OF PALLADIUM(II) AS ITS DIMETHYDIOXIME COMPLEX

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A new, cylindrical silver-based amalgam film electrode (Hg(Ag)FE) of prolonged analytical application has recently been introduced for voltammetric measurements and has been applied for the determination of Pb, Zn, Cd, Cu, Cr, Ni and Co by means of stripping voltammetry[1,2,4] and stripping chronopotentiometry[3]. The electrode design enables easy and quick regeneration of the liquid layer before each measurement cycle and, consequently, good reproducibility of results. The paper features a description of a sensitive adsorptive stripping voltammetric protocol for palladium(II) determination in the presence of dimethylglyoxime (DMG) at an amalgam film electrode (Hg(Ag)FE) of prolonged analytical applicability. The procedure is based on the adsorptive preconcentration of the Pd(II)-dimethylglyoxime complex onto the (Hg(Ag)FE) at –0.55 V, followed by a negatively-going

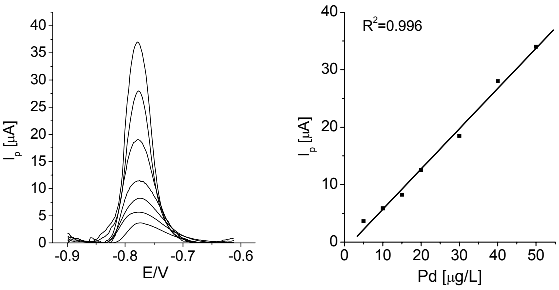

Fig. 1. **The SW-AdSV curves of Pd for successively increased concentrations of palladium in the range from 5 to 50 μg L$^{-1}$** (obtained after subtraction of the background curve). Inset: calibration plot. Supporting electrolyte: 0.1 M acetate buffer (pH 4.4), 0.2 mM DMG. $E_{dep} = -0.55$ V, $t_{dep} = 60$ s

square-wave voltammetric scan. Factors affecting the stripping performance, such as the composition of the supporting electrolyte, including different ligands, DMG concentration, pH, potential and time of preconcentration, type of voltammetric mode, SW pulse amplitude and electrode surface have been investigated and optimized. The optimized procedure yields favorable and highly stable stripping responses with good precision (RSD = 3.0 % for a Pd concentration of 2.0 μg L$^{-1}$), a low detection limit (0.13 μg L$^{-1}$ for a Pd concentration of 0.3 μg L$^{-1}$ Pd(II)), and good linearity (from 0.5 μg L$^{-1}$ up to 100 μg L$^{-1}$, $R^2 = 0.996$, Fig. 1) for a deposition time of 60 s. Possible interferences from coexisting ions and surface active substances were also studied.

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REFERENCES

1. Baś B., Kowalski Z.: Electroanalysis *14*, 1067 (2002).
2. Baś B.: Anal.Chim. Acta *570*, 195 (2006).
3. Kapturski P., Bobrowski A.: Electroanalysis *19*, 1863 (2007).
4. Kapturski P., Bobrowski A.: J. Electroanal. Chem., doi:10.1016/j.jelechem.2008.01.007 (2008).

## PP015

## A CATALYTIC ADSORPTIVE STRIPPING VOLTAMMETRIC PROCEDURE FOR HEXAVALENT CHROMIUM DETERMINATION IN PORE AND OVERLYING WATER

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Catalytic Adsorptive Stripping Voltammetry (CAdSV) has proved to be useful in the determination of Cr(VI) with a very low detection limit in different water samples including rain[1], sea[2], river[2,3], lake[2,3] water and landfill leachate[4]. The method is based on the accumulation of the Cr(III)-DTPA complex formed instantaneously from the very active Cr(III) ions generated by the reduction of Cr(VI) at the electrode surface, and the utilization of the catalytic reaction in the presence of nitrate ions[2]. One of the main reasons why the application of electrochemical methods to the analysis of real samples has not always been successful is the inevitable presence of surface active substances (SAS). Depending on their concentration and type, SAS can partially or completely suppress the observed chromium voltammetric signal. In particular, overlying and pore water samples from natural aquatic systems often contain high concentrations of organic matter (up to 160 mg L$^{-1}$) coupled with low concentrations of chromium (less than 1 μg L$^{-1}$ Cr(VI)), thus Cr(VI) determination is exceptionally difficult. This paper features a description of a new protocol for Cr(VI) determination in pore and overlying water samples.

In this work, well-known voltammetric procedures for the determination of chromium with DTPA and nitrate[1–4] have been adopted for the Cr(VI) quantification in the presence of an excess of SAS. This task was achieved by means of a selective separation of organic matter on Amberlite XAD-7 (ref.[5]) resin. The SAS were separated directly in the voltammetric cell by adding Amberlite XAD-7 (ref.[6]) and stirring the solution for 5 min before determination. The difference in CAdSV curves with and without separation is illustrated in Fig. 1. The procedure was applied in hexavalent chromium analysis in pore and overlying water samples collected in the upper Dunajec river and the Czorsztyn reservoir (Poland). The results obtained using the elaborated method were confirmed by those achieved by the CAdSV procedure based on matrix exchange in the flow system[7].

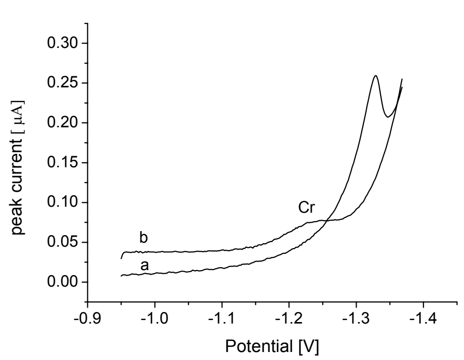

Fig. 1. **CAdS voltammograms obtained for overlying water sample**. Supporting electrolyte: 0.1 M acetate buffer, 0.25 M $KNO_3$, 0.01 M DTPA; pH 6.2 (a); Curve (b) – with addition of 0.6 g XAD–7 (5 min adsorption with stirring). $E_{acc} = -0.95$ V; $t_{dep} = 15$ s

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REFERENCES
1. Golimowski J., Valenta P., Nuernberg H. W: Fresenius' Z. Anal. Chem. *322*, 315 (1985).
2. Boussemart M., van den Berg C. M. G., Ghaddaf M.: Anal.Chim. Acta *262*, 103 (1992).
3. Bobrowski A., Dominik J., Niewiara E., Szalińska E., Vignati D., Zarębski J: Talanta *63*, 1003 (2004).
4. Li Y., Xue H.: Anal. Chim. Acta *448*, 121 (2001).
5. Petting M., Capri S.: Anal. Chim. Acta *540*, 239 (2005).
6. Grabarczyk M.: Anal. Bioanal. Chem. *390*, 979 (2008).
7. Korolczuk M., Grabarczyk M.: Anal. Chim. Acta *387*, 97 (1999).

## PP016

## ELECTROCHEMICAL AND MICROSCOPIC CHARACTERISTICS OF A LEAD-MODIFIED CARBON PASTE ELECTRODE

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Carbon electrodes plated with metal films have been the subject of investigation for many years. Recently, the electrochemically plated lead layer was examined as the prospective electrodes' modifier[1,2]. The interest in this material was inspired by the possibility of plating the lead film on the support surface *in situ*, in fairly alkaline media. *In-situ* plating indisputably simplifies and shortens the experimental procedure for adsorptive stripping voltammetry, where work in such media is routine. The aim of this work is to show that a lead film plated *in situ* at a carbon paste support could work as the electrode for the adsorptive stripping voltammetric determination of cobalt traces in an ammonia buffer solution.

To show the applicability of the new electrode, a catalytic adsorptive Co system in a supporting electrolyte containing 0.1 M ammonia buffer, $5\times10^{-4}$ M nioxime and 0.25 M nitrite was selected and investigated. Pb and Co ions were simultaneously accumulated *in situ* on the electrode surface. The lead layer was deposited electrochemically after applying the potential of −1.3 V ('nucleation potential') and then at −0.75 V, at which potential also the Co(II)-nioximate complex was pre-concentrated via adsorption. Instrumental parameters, such as the time of nucleation and formation of Pb film deposits, the time of accumulation of the Co-nioxime complex at the PbF/CPE, and the procedures of electrode regeneration, were optimized to obtain good reproducibility and sensitivity of the Co response. The optimized procedure yields favorable and highly stable stripping responses with good precision ($RSD$ = 3 % for a $5\times10^{-8}$ M Co) and good linearity (up to $5\times10^{-7}$ M, coefficient of determination, $R$ = 0.996). The detection limit was $4\times10^{-10}$ M Co (0.023 μg L$^{-1}$) for an accumulation time of 120 s. The described method enables Co determination in the presence of a high excess of Ni or Zn. Finally, the voltammetric data were correlated with structural characterization by means of scanning electron microscopy (SEM) and X-ray fluorescence spectroscopy (XRF).

*Financial support from the Ministry of Science and Higher Education (project N507 063 32/1767) is gratefully acknowledged.*

REFERENCES
1. Korolczuk M., Tyszczuk K., Grabarczyk M.: Electrochem. Commun. *7*, 1185 (2005).
2. Grabarczyk M., Korolczuk M.: Electroanalysis *18*, 70 (2006).

## PP017

## DEVELOPMENT OF AMPEROMETRIC PUTRESCINE BIOSENSOR FOR FOOD ANALYSIS

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Biogenic amines are organic bases with low molecular weight and biological importance. Although they are essential for all living cells, consumption of food containing high amounts of them may have toxicological effects. The analysis of biogenic amine content of foodstuff gives information about the potential health risk and quality, since high level in non-fermented foods indicates undesired microbial activity during food processing and storage[1].

The aim of our work is to develop an enzyme based-amperometric biosensor applicable as food quality marker. This biosensor selectively measures putrescine which can be considered as an indicator of microbial spoilage. Putrescine oxidase (EC 1.4.3.10) was isolated from *Kocurea rosea* (*Micrococcus Rubens*) by an improved and simplified purification procedure[2] in our laboratory. Cells were grown on brain heart infusion medium supplemented with putrescine. Cell-free extract was prepared in pH 8.0 Tris buffer by Bead-beater and purified with three-phase partitioning (TPP), DEAE-cellulose chromatography and ultrafiltration steps.

Our putrescine biosensor works in flow injection analysis system (FIA) using a potentiostat (QuadStat 164, eDAQ, Australia). Evaluation of measured data was done with eDAQ e-corder A/D converter and eDAQ Chart software.

The enzyme was immobilized on the surface of a spectroscopic graphite electrode in redox hydrogel with horseradish peroxidase, Os mediator and poly(ethylene glycol) (400) diglycidyl ether (PEGDGE) as crosslinking agent[3,4]. This modified working electrode was used in wall-jet type amperometric cell together with the Ag/AgCl (0.1 M KCl) reference electrode and a platinum wire as counter electrode. The effect of hydrogel composition, pH and potential dependence were studied, the range of linear response was determined and real food samples were analyzed.

*This study was supported by EgerFood Regional Knowledge Center application 9/2005.*

REFERENCES
1. Silla Santos M. H.: Int. J. Food Microbiol., 29213-231, (1996).
2. DeSa R. J.: J. Biol. Chem. *247*, 5527 (1972).
3. Bott A. W.: Cur. Separ. *21*, 3 (2004).
4. Ruzgas T.: Anal. Chim. Acta *1996*, 123.

## PP018

## PORTABLE ELECTROCHEMICAL URIC ACID MONITORING SYSTEM BASED ON SCREEN-PRINTED ELECTRODES

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Uric acid(UA, 7,9-dihydro-1*H*-purine-2,6,8(3*H*)-trione) is the major end product of purine metabolism. Purines from catabolism of dietary nucleic acid are converted to uric acid directly. However, the most of purines excreted as uric acid arises from degradation of endogenous nucleic acids. Its determination serves as a marker for the detection of disorders associated with purine metabolism such as gout arthritis, Lesch-Nyhan syndrome and renal retention. Also, hyperuricemia may indicate other diseases mainly related with cell degradation such as chemotherapy of malignant tumors as leukemias or lymphomas. Diagnosis of these clinical disorders are carried out by monitoring UA blood or urinary levels. The normal UA serum levels range from 3.5–7.2 mg $dL^{-1}$ in men and from 2.6–6 mg $dL^{-1}$ for women.

Methods in current use for measuring uric acid fall into two groups: phosphotungstic acid methods and uricase methods.

Phosphotungstic acid methods rely on the reduction of this acid by urate in alkaline medium to give a blue color in solution (tungsten blue) that is read spectrophotometrically at wavelengths of 650 to 700 nm.

Uricase methods are inherently more specific than colormetric methods. In this case urate oxidation is catalyzed by the enzyme uricase to allantoin and hydrogen peroxide. These methods became feasible and popular as a result of availability of high quality, low-cost preparations of the bacterial enzyme.

HPLC methods using reversed-phase columns have also been used to measure uric acid.

Some electrochemical methods based on enzymatic and non enzymatic approaches have been already reported for UA analysis[1,2]. Electrochemical activated surfaces, carbon nanotube and redox mediator modified electrodes can be used for the enhancement of the oxidation UA analytical signal.

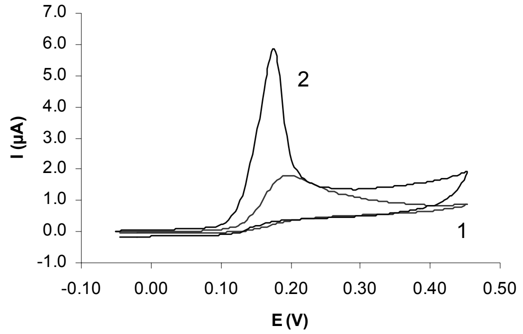

Fig. 1. **Cyclic voltammograms of uric acid $5\times10^{-5}$ M in 0.1 M AcO- buffer solution pH 5,0; $\nu$=50 mV $s^{-1}$**. (1) Red line: screen-printed carbon electrode, (2) blue line: multi walled carbon nanotube modified screen printed electrode

A trend in the development of electrochemical sensors for decentralized analysis is the miniaturization of the analysis device and the instrumentation. Therefore in this work screen printed electrodes are evaluated for the detection of uric acid in combination with a hand held potentiostat.

Different carbon screen-printed electrodes are evaluated (Fig. 1) and biological fluids as urine and blood are analysed through voltammetric techniques. Furthermore, the proposed analysis system is compared with clinical serum analysis carried out by enzymatic method.

REFERENCES
1. Zen J. M., Jou J.-J., Hangovan G.: Analyst *123*, 1345 (1998).
2. Bravo R., Hsuch C., Jaramillo A., Brajter-Toth A.: Analyst *123*, 1625 (1998).

## PP019

## DOUBLE-TAGGING PCR AND GOLD NANOPARTICLES USED IN IMPEDIMETRIC GENOSENSING

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Real sample DNA analysis is proposed employing an electrochemical impedimetric genosensor, previously developed in our laboratories[1], applied to double stranded DNA sequences produced by the polymerase chain reaction (PCR) amplification.

Electrochemical Impedance Spectroscopy is a rapid developing technique for the transduction of biosensing events at the surface of an electrode[2]. Transduction principle exploits changes in interfacial resistance of charge transfer after modification of the genosensing transducer with DNA[3].

In the present work, an avidin bulk-modified graphite-epoxy biocomposite (Av-GEB) was employed to immobilize –onto the electrode surface– the double-tagged DNA, modified in each end with biotin and digoxigenin, respectively. Impedance spectra were recorded to detect the change in interfacial charge transfer resistance ($R_{ct}$) as observed from the ferri/ferrocyanide redox marker reaction. A further step in the genosensing procedure was the amplification of impedimetric signal by the use of gold nanoparticles modified with Anti-Mouse IgG (whole molecule)–Gold antibody. The latter were immobilized to the digoxigenin-modified end of the amplicon by a monoclonal IgG1kappa anti-Digoxigenin antibody from mouse.

Results obtained by the comparison of Rct values after each further modification of the electrode surface show a significant difference in the impedimetric signal variation between experiments and negative controls. Moreover, this difference results thoroughly amplified thanks to the procedure used for signal enhancement.

The sensitivity of the technique and the good reproducibility of results confirm the validity of this method based on a universal affinity biocomposite platform coupled with the impedimetric technique. The described strategy was used for the rapid and sensitive detection of PCR amplified samples of *Salmonella spp*, the most important pathogen affecting food safety.

REFERENCES

1. Bonanni A., Pividori M. I., del Valle M.: Anal. Bioanal. Chem. *389*, 851 (2007).
2. Berggren C., Stålhandske P., Brundell J., Johansson G.: Electroanalysis *11*, 156 (1999).
3. Katz E., Willner I.: Electroanalysis *15*, 927 (2003).

## PP020
## ELECTROCHEMICAL METHOD FOR EVALUATION OF OXIDANT/ANTIOXIDANT ACTIVITY OF BIOLOGICAL FLUIDS

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Free-radical oxidation, on the one hand, ensures the normal progress of metabolism processes in the organism, but, on the other hand, the disturbance of the oxidant/antioxidant balance leads to the oxidation stress, which is a disbalance between the generation of active forms of oxygen and the antioxidant protection of the organism. Surplus active forms of oxygen can destroy lipids of cells, proteins or DNA, inhibiting the normal functioning of the organism.

The total antioxidant activity of a sample should be considered as an integral parameter. We have proposed a method involving the use of a mediator system and measurements of the potential across a screen-printed platinum sensor as the source of information about the antioxidant/oxidant activity of test materials.

The proposed potentiometric method for measurement of the antioxidant activity is a promising alternative choice against the available methods. The subjects of study were seminal and follicular fluids.

The optimal concentrations of the oxidized and reduced forms of the mediator system were determined for each of the aforementioned test fluids. The sampling and sample handling methods were selected. It was shown that the devised potentiometric method is highly informative and provides reliable results.

The proposed method has the advantages of simplicity and a low cost. The obtained data suggest that the aforementioned parameter of the antioxidant activity can be used as a criterion for evaluation of the general antioxidant activity of the seminal and follicular fluids and serve as an index pointing to the condition of the reproductive function in humans.

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## PP021
## AMPEROMETRIC GLUCOSE BIOSENSOR BASED ON ELECTROPOLYMERIZED CARBON NANOTUBE/ POLYPYRROLE COMPOSITE FILM

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An important work in the design and fabrication of biosensors is to find an effective immobilization method, an appropriate support material and a fast and simple procedure. Thus, we report a one-step preparation route of amperometric enzyme electrodes based on incorporating a carbon-nanotube (CNT) dopant and the enzyme within an electropolymerized polypyrrole (PPY) film.

Because electropolymerization represents an attractive wellcontrolled one-step procedure for preparing amperometric enzyme electrodes[1,2], the nanocomposite films were electrochemically synthesized by electrooxidation of pyrrole in an aqueous solution containing appropriate amounts of GOD and CNTs. The main advantages of this immobilization way are the simple one-step preparation, exclusion of electroactive interferences, control of the film thickness, and localization of enzymes onto electrode surfaces[3–5]. The electropolymerization was carried out at a pH above the isoelectic point of the protein in order to provide a negative charge. The relevant parameters of the film preparation were examined and optimized. The amperometric detection of glucose was assayed by potentiostating the enzyme electrode at a potential to reduce the enzymatically produced $H_2O_2$ with minimal interference from the coexisting electroactive compounds. The results indicate that the PPY-CNTs-GOD nanobiocomposite film is highly sensitive and suitable for glucose biosensor function.

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REFERENCES
1. Emr S. A., Yacynych A. M.: Electroanalysis *7*, 913 (1995).
2. Trojanowicz M., Krawczynski T.: Mikrochim. Acta *121*, 167 (1995).
3. Zhang S., Wright G., Yang Y.: Biosens. Bioelectron. *15*, 273 (2000).
4. Wu X. J., Chio M. M. F.: Anal. Chem. *76*, 4279 (2004).
5. Puig-Lleixa C., Jimenez C., Bartroli J.: Sens. Actuators, B *72*, 56 (2001).

## PP022

## MODIFIED ELECTRODES OBTAINED BY ELECTRODEPOSITION OF POLYMERIC AND COMPOSITE FILMS ON WOLFRAM SURFACE ELECTRODE

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Polypyrrole, polyaniline films and polypyrrole-polyaniline composite films were obtained by electrochemical oxidation of the monomers: pyrrole, aniline and pyrrole-aniline mixture of different compositions in aqueous solutions containing different dopant anions as supporting electrolyte.

Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were used to investigate the electrochemical properties of modified electrodes. The results indicate that the surfactant anions favour redox processes which are faster and more reversible than those associated to the usual polymeric electrodes. In fact, while in polymeric films doped by conventional, small anions (e.g. $Cl^-$), the charge compensation is assured by uptake of the anions during oxidation and the release of the same anions during reduction, in the polymeric films prepared in the presence of the large–anions salts (e.g. SDS, AOT) the charge compensation appears to involve incorporation of cations since the large anions are not easily released from the polymer matrix.

Multilayered coatings, consisting of combinations of the conducting polymers polyaniline (PANI) and polypyrrole (PPY) were deposited onto wolfram by different electrochemical techniques, such as potentiodynamic, galvanostatic and potentiostatic modes. The overall system has a bilayered structure, indicating that the electrochemical interface during polymers electrodeposition might be situated at the polypyrrole-solution interface in case of PANI/PPY wolfram electrode, respective the polyaniline-solution one in the case of PPY/PANI wolfram electrode. The presence of the surfactant (SDS or AOT) makes easier the pyrrole and aniline electropolymerization. Indeed, the presence of micelles decreases the monomer oxidation potential and induces an acceleration of the polymerization. In the used electrosinthesys solution pyrrole and aniline have approximative the same monomer oxidation potentials. Therefore, an electropolymerization mixture of these monomers was carried out with different ratios in order to prepare copolymers and the resulting products were characterized by electrochemistry, IR and IV-visible spectroscopy and SEM.

REFERENCES
1. Akundy G. S., Rajagopalan R., Iroh J. O.: J. Appl. Polym. Sci. *83*, 1970 (2002).
2. Branzoi V., Pilan L., Golgovici F., Branzoi F.: Mol. Cryst. Liq. Cryst. *446*, 305 (2006).

## PP023

## NANOCOMPOSITE FILMS OBTAINED BY ELECTROCHEMICAL CO-DEPSITION OF CONDUCTING POLYMERS AND CARBON NANOTUBES

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The electrochemical growth of carbon nanotubes (CNTs) – conducting polymer composites offers the ability to produce tree-dimensional nanostructured films that combine the redox pseudo-capacitive charge storage mechanism of conducting polymers with the high surface area and conductivity of CNTs[1–6]. Nanocomposite films of CNTs and either polyaniline (PANI) or polypyrrole (PPY) were prepared using electrochemical polymerization technique in which nanotubes and conducting polymer were deposited simultaneously from solutions containing acid treated CNTs and the corresponding monomer. The electropolymerization process was carried out by galvanostatic method. The concentration and dispersion of CNTs in polymerization electrolyte, in addition to any supporting electrolyte used, were found to have a significant effect on thickness of the composite film and CNTs loading in the produced films. Electrochemical impedance spectroscopy (EIS), cyclic voltammetry and square wave voltammetry were used to investigate the electrochemical properties of the composite films. The electrochemical response, both in cyclic voltammetry and square wave voltammetry is significantly increased for the composite films in comparison with the respective polymers alone. The EIS on CNTs/PPY and CNTs/PANI composite electrodes were carried out in the supporting electrolyte in dependence of the following parameters: film thickness, supporting electrolyte concentration, temperature and polarisation potential.

REFERENCES
1. Hughes M., Chen G. Z., Shaffer M. S. P., Fray D. J., Windle A. H.: Chem. Mater. *14*, 1610 (2002).
2. Hughes M., Shaffer M. S. P., Renouf A. C., Singh C., Chen G. Z., Fray J.: Adv. Mater. *14*, 382 (2002).
3. Hughes M., Chen G. Z., Shaffer M. S. P., Fray D. J., Windle A. H.: Comp. Sci. Techn. *64*, 2325 (2004).

4. Chen G. Z., Shaffer M. S. P., Coleby D., Dixon G., Zhou W., Fray D. J., Windle A. H.: Adv. Mater. *12*, 522, (2000).
5. Wu M., Snook G. A., Gupta V., Shaffer M., Fray D. J., Chen G. Z.: J. Mater. Chem. *15*, 2297 (2005).
6. Peng C., Jin J., Chen G. Z.: Electrochim. Acta *53*, 525 (2007).

## PP024

## DETERMINATION OF THEOPHYLLINE AT A GLASSY CARBON ELECTRODE MODIFIED BY ELECTRODEPOSITED CYSTEIC ACID

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It was recently shown that glassy carbon electrodes (GCE) modified with cysteic acid can be successfully used in the determination of nimesulide[1] and other analytes of pharmaceutical interest[2] thanks to their electrostatic accumulation onto the modified electrode surface. Cysteic acid was deposited onto the GCE surface by electrochemical oxidation of cysteine by mean of cyclic voltammetry.

In this work, such modified GCE are used for determining methylxanthines, with particular attention to theophylline. According to several Authors, common GCE don't allow acquiring sufficiently reproducible results in the determination of these analytes. This because their oxidation occurs at very positive potentials, overlapping with the discharge of the background medium[3]. Several solutions were proposed, including the use of electrodes with a wider anodic potential range[3] or modified electrodes[4], or unusual combination of solvent/supporting electrolyte[5]. Cysteic acid modified electrodes appear to be a straightforward solution to the problem, thanks to their affinity to the above mentioned analytes, the low cost, the simplicity of the modification procedure and the reproducibility of the electrode surface.

Preliminary cyclic voltammetric experiments were made to evaluate the influence of the supporting electrolyte and of the electrodeposition parameters (cysteine concentration, scan rate, potentials, etc).

Differential pulse voltammetry experiments allowed to estimate the linear range, the calibration function and the limit of detection. The results confirmed the potentiality of the modified electrode, characterized by higher sensitivity, selectivity and reproducibility in comparison to unmodified GCE.

The possible interferences when analyzing real samples were also considered. The results are discussed in the light of the most recent literature information.

REFERENCES

1. Wang C. Y., Shao X., Qingxiu L., Qu Q., Yang G., Hu X.: J. Pharm. Biomed. Anal. *42*, 237 (2006).
2. Wang C. Y., Wang Z. X., Guan J., Hu X. Y.: Sensors *6*, 1139 (2006).
3. Spataru N., Sarada B. V., Tryk D. A., Fujishima A.: Electroanalysis *14*, 721 (2002).
4. Zen J.-M., Ting Y.-S., Shih Y.: Analyst *123*, 1145 (1998).
5. Lau O.-W., Luk S.-F., Cheung Y.-M.: Analyst *114*, 1047 (1989).

## PP025

## IMPROVEMENT OF STORAGE STABILITY FOR AMPEROMETRIC BIOSENSORS BASED ON ALCOHOL OXIDASE IMMOBILIZED BY ENTRAPMENT IN A PHOTOPOLYMERISABLE MATRIX

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One important impediment for successful commercial application of enzymatic biosensors is their limited storage stability caused to the instability of the used biocomponent As model enzyme was used alcohol oxidase (AOX), a model enzyme with a poor storage stability. The detection was made by cronoamperometry in a drop of solution and the transducers were screen-printed electrodes modified with mediator Co-phthalocyanine. The enzyme was immobilized onto screen-printed electrodes by entrapment in a photopolymerisable PVA matrix, a method that already provides a stabilizing effect.

The storage stability of immobilized AOX was improved by the use of three different stabilizers: sorbitol, Tween 20 and PEG 6000 and compared with the enzyme immobilized without stabilizers.. All stabilizers have a positive effect on the enzyme stability. The increase of storage time in comparison with biosensors without stabilizers was by 25 % for Tween 20 while the sorbitol allow a double storage time of the biosensors. The most appropriate stabilizer proved to be PEG 6000 that allowed the increase of the storage time of the biosensors by more than 3 times.

*This work was supported by Romanian Ministry of Education and Research through Grant CEEX-156/2006 (BAME).*

REFERENCES

1. Bucur B., Radu G. L., Toader C. N.: Eur. Food Res. Technol. in press.
2. Bucur B., Mallat E., Gurban A. M., Gocheva Y., Velasco C., Marty J. L., Noguer T.: Biosens. Bioelectron. *21*, 2290 (2006).
3. Bucur B., Bucur M. P., Radu G. L.: Rev. Chim *58*, 1145 (2007).

## PP026
## TYROSINASE BASED AMPEROMETRIC BIOSENSORS FOR THE DETERMINATION OF L CYSTEINE

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An amperometric biosensor for the determination of cysteine was developed by immobilisation of tyrosinase on screen-printed electrode (SPEs) using the sol-gel technique. The detection was made by amperometry in stirred solution.

The enzymes were immobilized on surface of working electrode by entrapment in a sol-gel matrix that is composed of tetramethoxysilane and methyltrimethoxysilane[1,2]. A Nafion polymer layer was used to improve the operational stability.

All measurements were carried out at a fixed potential of –150 mV *vs* Ag/AgCl. Experimental parameters such as the pH of the measuring solution, response time, enzyme loading, immobilization protocol were optimized using 50 μM catechol as substrat. A good reproducibility and operational stability were found for tyrosinase biosensors (10 UI/electrod) in 0.1 M phosphate buffer/0.1 M KCl, pH 6.5.

Cysteine was determined by the inhibition of the tyrosinase. The enzyme is sensitive to thiols and thus it is possible to selectively determine cysteine from complex samples[3].

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REFERENCES

1. Kim A. M., Lee W. Y.: Anal. Chim. Acta *479*, 143 (2003).
2. Bucur B., Fournier D., Danet A., Marty J. L.: Anal. Chim. Acta *562*, 115 (2006).
3. Vieira I. Da Cruz, Filho-Fatibello O.: Anal. Chim. Acta *399*, 287 (1999).

## PP027
## CARBON-CONTAINING ELECTRODES MODIFIED BY SILVER NANOPARTICLES

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Nanomaterials are finding increasing use for electrochemical sensors. Therefore it becomes topical to perform systematic and comprehensive studies of electrochemical properties of nanoparticles and nanostructures.

The goal of this work was to study specific features of the electrochemical behavior of silver nanoparticles depending on their size, methods of production and immobilization on different types of carbon-containing substrates.

Silver nanoparticles of different sizes were prepared by chemical and electrochemical reduction from silver nitrate solutions. Chemically synthesized nanoparticles were immobilized on the electrode surface by adsorption from a silver sol solution or by depositing a droplet of this solution in the working zone.

In accordance with the theory of different energy states of a metal on an indifferent electrode, the energy state of the metal was characterized by the parameter $I_{max}/Q$ (ref.[1]), which is the ratio of the maximum current of the metal ionization ($I_{max}$) to the quantity of electricity consumed in the ionization process (Q).

It was found that sorption of fine particles was faster and their parameter $I_{max}/Q$ was much larger than they were for coarse particles. The parameter $I_{max}/Q$ decreased with increasing sorption time, probably pointing to the aggregation of the particles and the formation of a phase layer. It was shown that the electrochemical activity of silver particles was enhanced upon dilution. The comparison of the three methods used for immobilization of the particles on the electrode surface demonstrated that their reactivity was better in the sorption method than in the droplet and electrochemical methods.

From the study optimal conditions for production of electrodes with silver nanoparticles for determination of anions were selected. It was shown that the electrodes with the sorption-modified surface provided the best sensitivity.

*The authors are very grateful to RFBR for the financial support (projects No. 07-03-96070-p_ural_a).*

REFERENCE

1. Brainina Kh., Neiman E.: *Electroanalytical Stripping Methods*. J. Wiley & Sons, USA 1993.

## PP028
## CONTINUOUS MONITORING OF ZINC, IRON AND COPPER IN POLLUTED RIVER WATER, SPECIATION ANALYSES

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In this contribution we present an automatic voltammetric system using solid silver amalgam electrode for continuous and on-line remote monitoring of heavy metals in polluted river water with only minor maintenance of the system. It consists of two cabinets: (*i*) Cabinet 1 containing an industry PC with a DAQ card for logging data from the measurements and; (*ii*) Cabinet 2 containing the voltammetric cell and sensor interface system, power supply and relays for controlling external devices like drain valve, main water pump for collecting sample, an agitation equipment and dosage pump for adding supporting electrolyte.

Using this system, concentrations of zinc, iron[1] and copper have been monitored every 60 minutes by DPASV over a period of 4 months in two different rivers in Norway contaminated by former mining activities. Overall, high concentrations of these dissolved metals were indeed abnormally high for natural aquatic systems because of a continuous leaching of remaining ores into the river. Maintenance was also more intensive when concentrations of iron (II) in the samples were higher than dozens of ppb because of iron (III) hydroxides deposition on the sensor within a few days.

Additionally to the automatic voltammetric monitoring, physico-chemical parameters like pH and conductivity have been measured[2], and samples have also been collected periodically manually in order to determine total concentrations of dissolved and particulate trace metals by using a high resolution ICP-MS. Furthermore, DGT (Diffusive Gradients in Thin Films) probes have also been deployed for quality assurance consideration and for obtaining complementary information on trace metal speciation. Overall, all these results have permitted to set up an advanced monitoring strategy for metallic pollutants and a whole discussion on metal behaviors in these two sites as well.

REFERENCES

1. Mikkelsen Ø., Schrøder K. H.: Electroanalysis *16*, 386 (2004).
2. Mikkelsen Ø., Skogvold S. M., Schrøder K. H.: Electroanalysis *17*, 431 (2005).

## PP029

## THE NATURAL DIATOMITE FROM CALDIRAN-VAN (TURKEY): ELECTROANALYTICAL APPLICATION AT MODIFIED CARBON PASTE ELECTRODE

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Diatomite is regarded as a mineral of organic origin, where the silica of fossilised diatom skeleton resembles opal or hydrous silica in composition ($SiO_2 \cdot nH_2O$). In recent years, successful applications of silica-based materials in the field of modified electrode have increased exponentially. However, despite its strong adsorption capacity, high porosity, resistance to chemicals, thermal stability and high purity, the use of diatomite in connection with the electroanalysis has not been attempted and no reference is mentioned in literature.

In this research, the use of diatomite of Van/Caldiran region in Turkey, whose physical, chemical, mineralogical and micro-structural tests were also carried out, was described for the electroanalytical application of chemically modified electrode. For this purpose, the determination of Naratriptan which is a novel oral triptan (serotonin, 5-hydroxytryptamine receptor agonist) in migraine treatment, by means of a carbon paste electrode modified with 10 % (w/w) of diatomite was studied using cyclic and square-wave voltammetry. Very few analytical techniques for the determination of Naratriptan are described. These reported methods are not spesific for the drug and time-consuming. To our knowledge, no information about the electrochemical redox properties of Naratriptan and its analytical application have appeared in the literature.

Naratriptan exhibited four pH dependent anodic steps (representing an irreversible oxidation). The experimental conditions that affect the electrode reaction process were studied in terms of pH of the supporting electrolyte, scan rate, accumulation variables and square-wave parameters. Using square-wave stripping mode, the drug yielded a well-defined voltammetric response in Britton-Robinson buffer, pH 4.0 at 0.84 V (*vs* Ag/AgCl) (a pre-concentration step being carried out with an open circuit at 120 s). The process could be used to determine Naratriptan concentrations in the range $5\times10^{-7}$–$9\times10^{-7}$ M, with a detection limit of $1.14\times10^{-7}$ M. The applicability of to direct assay of spiked human urine samples was illustrated.

## PP030

## IONIC LIQUID-CARBON NANOTUBES COMPOSITES FOR THE PREPARATION OF ELECTROCHEMICAL BIOSENSORS

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Ionic liquids (ILs) are characterized by the high conductivity and electrochemical stability in a wide potential window. They also give selectivity effects by partioning for specific ions[1]. Ionic interaction constitutes nowadays a simple, but also powerful aproach to immobilize biomolecules. The electro-static interaction between proteins and ILs adsorbed on the electrode surface has shown to affect significantly their electrochemical behaviour. Ionic functionalization of CNTs has been used to develop biocompatible CNTs for the preparation of bioelectrodes. ILs have also been used as a binder by mixing with graphite in preparing carbon paste electrodes[1]. This work describes the preparation and performance of a composite electrode based on multi-walled carbon nanotubes and 1-butyl-3-methyl-imidazoliumhexafluorophosphate, BMIM-$PF_6$-CNTs.

The electrodes were fabricated by hand mixing for 20 min of the required amounts of MWCNTs and ionic liquid to give a 30:70 CNTs: BMIM-$PF_6$ composition. Portions of the resulting mixture were then packed into Teflon holders (3 mm inner ø) and pressed tightly. The electrical contact was made through a stainless steel screw. Preliminary experiments using $H_2O_2$ as analyte for the optimization of experimental variables were carried out. The effect of the potential applied to the electrode on the steady-state currents from 0.5 mM $H_2O_2$ solutions in 0.05 M PBS of pH 7.4 was studied in the −0.8 to +0.8 V range. Significant anodic and cathodic currents were obtained, from +0.3 or −0.2 V respectively. The composition of the mixture was optimized by using electrodes prepared with different CNTs:BMIM-$PF_6$ ratios. Anodic currents were practically constant from 60 to 75 % IL, then decreasing up to 95% IL. EIS studies also revealed an increase in charge transfer resistance with the lower CNTs loading.

A good electroanalytical behaviour of the composite electrode towards the addition of $H_2O_2$ was observed. A linear calibration plot in the 7.5 μM to 3.2 mM concentration range was obtained with a slope of 10.4 mA/M, using +0.5 V as the detection potential. The achieved sensitivity is more than five times higher than that obtained with a Teflon-CNTs composite electrode. A LOD ($3s_b/m$) of 2.5 μM $H_2O_2$ and a good repeatability, with RSD = 5.3 % (n = 5) were obtained. The electrode has shown to be a useful matrix for the incorporation and direct electrochemistry of proteins/enzymes such as HRP, GOx or Cit c.

REFERENCES

1. Musameh M., Wang J.: Anal. Chim. Acta *606*, 45 (2008).
2. Du P., Liu S., Wu P., Cai C.: Electrochim. Acta *52*, 6534 (2007).

## PP031

## INTEGRATING ELECTROCHEMICAL DETECTION ON MICROCHIP ELECTROPHORESIS

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Miniaturized analytical systems, especially capillary electrophoresis microchips (MCE), have gained a great interest in the last decade. Among the detectors used for microchip capillary electrophoresis (MCE), electrochemical detection (ED) has proven to be very effective due to characteristics such as inherent miniaturization, sensitivity, low cost, portability and compatibility with microfabrication technology.

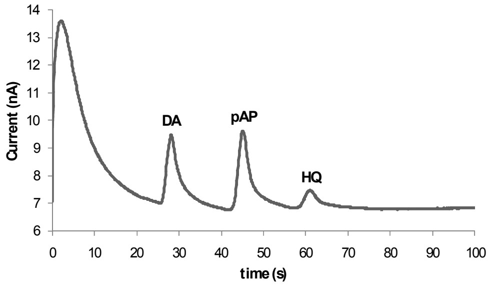

Fig. 1. **Electropherogram for the separation of a mixture containing DA, pAP and HQ** 100 μM using an SU-8 microchip with an integrated Pt thin-film detector

Different configurations can be used to integrate the electrochemical detection on microchips: in-channel, off-channel and end-channel. An end-channel configuration, where the working electrode is situated at the outlet (10-20 μm) of the separation channel, has been employed in this work.

The working electrode can be externally aligned using an off-chip approach. Nowadays this configuration is being used in conjunction with commercial microchips. Thus, a gold wire electrode has been aligned through a guide-channel practiced at the end of the separation channel. However, in this configuration the electrodes are not completely integrated.

Hence, an on-chip approach has been also used in combination with SU-8 microchips. The detector based on platinum thin-films has been integrated on-chip during the fabrication process of microchips.

Thus, two different microchip designs have been developed with three- (single-channel microchip) or four- (dual-channel microchip) electrode configuration.

In the first case, two different electrochemical detector designs have been evaluated in combination with an SU-8 single-channel microchip. Thus, the influence of the electrode size has been studied on the single-channel SU-8 microchip. Main separation parameters for separation of dopamine (DA), *p*-aminophenol (pAP) and hydroquinone (HQ) have been determined (Fig. 1).

On the other hand, dual-channel (Π-design) SU-8 microchips have been also evaluated for separation of the neurotransmitters dopamine (DA) and epinephrine (EP). The influence of the injection format has been adequately studied in order to perform a simultaneous and reproducible separation.

REFERENCE

1. Castaño-Álvarez M., Fernández-Abedul M. T., Costa-García A.: Electrophoresis *28*, 4679 (2007).

## PP032

## COMPARATIVE STUDY BY ESI-MS, ISOTHERMAL TITRATION CALORIMETRY AND VOLTAMMETRY/ MULTIVARIATE CURVE RESOLUTION OF THE COMPETITIVE BINDING OF HEAVY METALS WITH PHYTOCHELATINS

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Among the protecting mechanisms of live organisms against the toxic metals is worth mentioning the biosynthesis of phytochelatins ($PC_n$). $PC_n$ are small cysteine-rich peptides, containing a primary structure $(\gamma\text{-Glu-Cys})_n\text{-Gly}$ ($n$ = 2–11), synthesized by eukaryotes for various cellular functions, notably protection against oxidative stress, metal detoxification and homeostasis[1]. Due to their high Cys-content, $PC_n$ bind metal ions by chelation through -SH. Fundamental studies of the competition between essential metals (as Zn) and toxic metals (as Cd) is of the highest interest for the understanding of many biochemical and environmentally relevant processes as, for instance, metal toxicity to phytoplankton assemblages and phytoremediation[2].

The competitive binding of $Cd^{2+}$ and $Zn^{2+}$ by the phytochelatin ($\gamma$-Glu-Cys)$_4$-Gly ($PC_4$) has been examined using several techniques. Electrospray Ionization Mass Spectrometry (ESI-MS) is used to determine the stoichiometries of the complexes, while voltammetric data analyzed by Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) allows one to not only trace the displacement induced by $Cd^{2+}$ or $Zn^{2+}$ in the binding of $Zn^{2+}$or $Cd^{2+}$, respectively, by $PC_4$, but also to obtain a complete overview of the processes involved. Isothermal Titration Calorimetry (ITC) is used to determine the related binding and thermodynamic parameters[3].

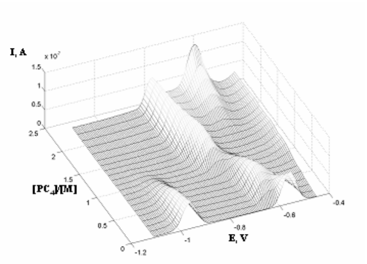

Fig. 1. **DPP curves for the titration of $Zn^{2+}$ and $Cd^{2+}$ equimolar solution**, in TRIS buffer at pH 7.4, with $PC_4$. Each metal concentration $1\times10^{-5}$ mol $L^{-1}$. On the plot [M] refers to $Zn^{2+}$ or $Cd^{2+}$ separately

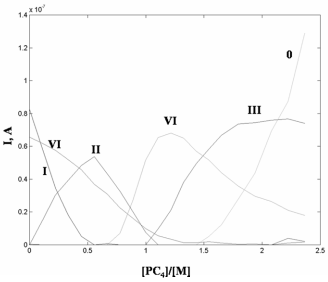

Fig. 2. **Concentration profiles obtained by MCR-ALS optimization of the experimental data set from Figure 1**, assuming 6 components and the constraints: non-negativity for both concentrations and signals, and signal-shape

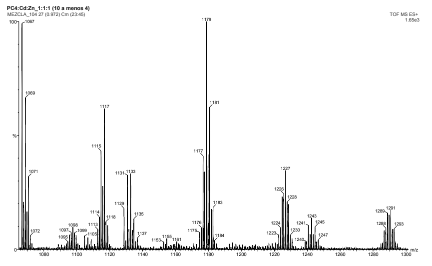

Fig. 3. **ESI-MS spectrum for a $Cd^{2+}$-$Zn^{2+}$-$PC_4$ solution at $10^{-5}$ mol $L^{-1}$ with 1:1:1 ratio in ammonium acetate/ammonium hydroxide buffer at pH 8**

From systematic metal-$PC_4$ titrations, such as the one shown in Figure 1, MCR-ALS allows one to obtain the concentration profiles of the different components (Fig. 2), and then propose a picture of the global process. These results can be confirmed and complemented by ESI-MS (Fig. 3) and ITC.

Our results prove that $Cd^{2+}$ is capable of displacing $Zn^{2+}$, either completely or partially, depending upon the $Cd^{2+}$-to-$Zn^{2+}$ ratio, and then forming mixed complexes. The formation of ternary $CdZn(PC_4)$ and $Cd_2Zn(PC_4)$ complexes has been observed[4].

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REFERENCES

1. Callahan D. L., Baker A. J. M., Kolev S. D., Wedd A. G.: J. Biol. Inorg. Chem. *11*, 2 (2006).
2. Wei L., Donat J. R., Fones G., Ahner B. A.: Environ. Sci. Technol. *37*, 3609 (2003).
3. Chekmeneva E., Prohens R., Díaz-Cruz J. M., Ariño C., Esteban M.: Anal. Biochem. *375*, 82 (2008).
4. Chekmeneva E., Prohens R., Díaz-Cruz J. M., Ariño C., Esteban M.: Environ. Sci. Technol. in press, 2008.

## PP033

## VOLTAMMETRIC DETERMINATION OF ANTIOXIDANTS IN MOTOR OILS USING GOLD WORKING ELECTRODE

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The antioxidant substances are added to the lubricant oils to prevent from the undesirable effects due to oxidative reactions. Secondary aromatic amines and phenols are the most often used additives, especially phenylalphanaphthylamine, alkylated diphenylamine, 2,6-di-tert-butyl-4-methylphenol (BHT).

The content of antioxidants closely relates to the wear degree of oils. This parameter is crucial to optimize the oil shelf life, it means mainly to determinate of oil exchange period, which is important from the economic and also environmental point of view. Two approaches for the antioxidants content in oils are described – FTIR spectroscopy and linear sweep voltammetry[1].

The aim of this work was to find the optimal conditions for the voltammetric determination of 2,6-di-tert-butyl-4-methylphenol (BHT) and to evaluate a method of its isolation from the oil matrix. With respect to the high reactivity of phenols in alkaline medium, the solution of 1M $H_2SO_4$ was used as a based electrolyte for the electrochemical oxidation of BHT. Acidic medium assures the sufficient stability of analyzed phenolic compounds. The electrode system consisting of a gold working electrode, silver/silverchloride referent electrode and carbon auxiliary electrode was used. The electrochemical oxidation was carried out using DC voltammetry in the potential range from 0 to 1200 mV. The wave corresponding to the BHT oxidation was observed between potential values 760–1050 mV. The wave high increased linearly with the analyte amount in the explored concentration range from 0.054 mg to 0.270 mg BHT in 20 ml of the analyzed solution. Isolation of BHT from oil matrix was realized using 96% ethanol extraction. The ultrasonic bath was applied for two minutes to improve the contact of both phases. Afterwards, the suspension was let to settle and the upper ethanolic layer was filtrated through the glass wadding. The obtained extract was used for the electrochemical analysis.

The designed methodology was tested on two real oil samples. The first one was newly produced with declared BHT amount of 200 mg kg$^{-1}$. The BHT concentration of 202.3 mg kg$^{-1}$ was determined in this sample. The second sample was two years old, also unused oil. Only 151.2 mg BHT per kg of oil was determined in this sample. Based on these results it is possible to say that the content of antioxidants in oils may decrease during the storage.

REFERENCE
1. ASTM D 6971 – 04.

## PP034
## CHARACTERIZATION OF ELECTRODEPOSITED PALLADIUM NANOPARTICLES AND NANOWIRES ON CARBON ELECTRODES

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Nanoparticles and nanowires of palladium electrodeposited on two types of carbon electrode, glassy carbon (GCE) and highly oriented pyrolytic graphite (HOPG), were studied by cyclic voltammetry (CV) and atomic force microscopy (AFM). The electrochemical behaviour of palladium observed was related to the palladium nanostructures electrodeposited at different potentials from a solution of palladium (II) sulphate, Fig. 1. The electrodeposition parameters, the concentration of the precursor solution and the topography of the carbon substrate influenced the morphology, size, shape and distribution of the palladium nanostructures electrodeposited.

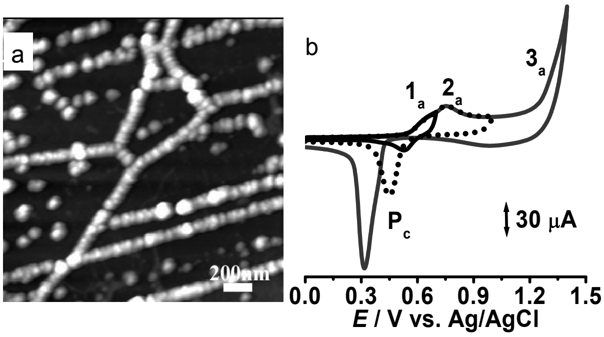

Fig. 1. **(a) AFM image in air of Pd(0) nanowires deposited onto HOPG. (b) CVs of 1mM $PdSO_4$ in pH 7.0 0.1 M phosphate buffer between 0.00 V and variable positive potential limits**

At negative applied potentials, Pd(0) nanowires, Fig. 1a, and nanoparticles were formed on the surface of the carbon electrodes, these nanostructures presenting characteristic redox processes. The formation of a palladium oxide pre-monolayer film begins at a negative potential, the phenomenon being strongly dependent on the size and morphological characteristics of Pd(0) nanostructures existent on the surface of the electrode.

Fig. 1b illustrates the different steps of Pd oxide layer formation, the application of a positive potential inducing the oxidation of the Pd(0) on the electrode surface.

This leads to the formation of a mixed oxide layer that may act as nucleation points for additional Pd metal growth, increasing the electrode surface coverage.

## PP035
## DEVELOPMENT OF A MICROELECTRODE ARRAYS SENSOR FOR HEAVY METAL ANALYSIS

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Because of their high toxicity, heavy metals like lead and cadmium spread in environment represent a risk for health even at μg L$^{-1}$ level. So their trace concentration in aqueous solution has to be successfully determined, with a special interest for their bioavailable forms, which are reported as particularly toxic[1].

In this way, our team develops disposable screen printed sensors of conventional size, modified by a mercury film. They have exhibited good limits of detection for lead and cadmium analysis without degassing and they have allowed an approach of speciation in real samples[2–4].

To improve this detection, microelectrode arrays have been achieved (Fig. 1). Their elaboration was easily realised

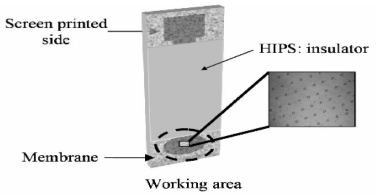

Fig. 1. **Representation of microelectrode arrays**

by combining femtolaser ablation of thin Mylar® sheets and screen printing technology.

The development of this type of sensor has a lot of advantageous characteristics. Therefore the sensitivity would be increased, we can especially work without stirring which can simplify the analytical device for on site-analysis. Furthermore, a lower amount of mercury was used to modify the electrode surface. The sensor performances could be improved with an optimization of key parameters like number, diameter or spacing between microelectrodes[5]. The robustness of this sensor has been evaluated by analysing of real samples.

REFERENCES

1. Van Leeuwen H. P., Town R. M., Buffle J., Cleven R. F. M. J., Davison W., Puy J., Van Riemsdijk W. H., Sigg L.: Environ. Sci. Technol. *39*, 8545 (2005).
2. Parat C., Betelu S., Authier L., Potin-Gautier M.: Anal. Chim. Acta, *573-574*, 14 (2006).
3. Betelu S., Parat C., Petrucciani N., Castetbon A., Authier L., Potin-Gautier M.: Electroanalysis *19*, 399 (2007).
4. Parat C., Authier L., Betelu S., Petrucciani N., Potin-Gautier M.: Electroanalysis *19*, 403 (2007).
5. Berduque A., Lanyon Y. H., Beni V., Herzog G., Watson Y. E., Rodgers K., Stam F., Alderman J., Arrigan D. W. M.: Talanta *71*, 1022 (2007).

## PP036

## METALLO-PHTHALOCYANINE MODIFIED CARBON PASTE ELECTRODES FOR THE DETERMINATON OF ANTIMALARIAL ARTEMISININ

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Artemisinin, a sesquiterpene endoperoxide, is a new potent, non-alkaloidal, antimalarial drug and is used in the therapy against the resistant strains of Plasmodium falciparum as well as cerebral malaria[1]. Artemisinin is isolated from the herb of the Chinese medicinal plant Artemisia annua, which seems to be the unique natural source of this drug[2]. Its quantity in the plant is usually in the range of 0.01–0.4 %, but some clones produce over 1 % dry weight[3].

The determination of artemisinin is a challenging issue as it is thermolabile and stains poorly because of the absence of chromophoric or fluorophoric groups. Moreover, artemisinin is sensitive against acid and base treatment, the concentration in the plant is low and various compounds in the crude plant extracts can interfere in its detection. Several analytical methods like TLC, HPLC, GC, CE, ELISA, SFC have been well adapted, however they have some limitations[3].

As artemisinin contains the electrochemically active endoperoxide (-O-O-) group, it can be reduced at various electrodes[4,5]. Modifying of electrodes provides the opportunity to improve the analysis of artemisinin concerning its selectivity and sensitivity. Due to this advantage the aim of our work was to investigate carbon paste electrodes bulk modified with metallo-phthalocyanines (cobalt, iron, manganese, and nickel) for the determination of artemisinin in Artemisia annua.

Best results for analysing artemisinin were obtained by using cobalt phthalocyanine as modifier. In Britton-Robinson buffer at pH 7 this electrode showed a significant catalytic activity in the presence of artemisinin at about −500 mV *vs.* Ag/AgCl by using cyclic and differential pulse voltammetry. Strict linearity between artemisinin concentration and peak height was observed in $2.7\times10^{-5}$–$6.4\times10^{-4}$ M concentration range ($R$ = 0.9998). The detection limit of artemisinin was calculated to be $9.2\times10^{-6}$ M. The developed electrode is applicable to determine artemisinin in complex plant materials.

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REFERENCES

1. Wernsdorfer H. W.: Expert Review of Anti-infective Therapy *2*, 181 (2004).
2. Qinghaosu Antimalarial Coordination Research Group: Chin. Med. J. *92*, 811 (1979).
3. Christen P., Veuthey J. L.: Curr. Med. Chem. *8*, 1827 (2001).
4. Katritzky Zhou Z. J., Yang P. H., Feng D. X., Zhu M. Y.: Yunnan Daxue Xuebao *25*, 144 (2003).
5. Debnath C., Haslinger E., Ortner A.: NPC *6*, 487 (2006).

## PP037

## CHLOROPEROXIDASE BASED ELECTROCHEMICAL SENSOR FOR TRICHLOROPHENOL

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Trichlorophenol and other chlorophenols are widely used in many industrial processes, such as the manufacture of plastics, dyes and pesticides. Owing to their toxicity, both the US Environmental Protection Agency (EPA) and the European Community (EC) have included some chlorophenols in their list of priority pollutants. Therefore, screening and monitoring of these pollutants are of great importance.

Chlorophenols can be determined by gas or liquid chromatography. Tyrosinase-based biosensors have also been used. Chloroperoxidase from *Caldariomyces Fumago* (CCPO) is a heme-thiolate enzyme with multifunctional activities typical of peroxidase as well as cytochrome P450 enzymes. Besides its primary function of chlorination, the ability of CCPO to catalyze the oxidative dehalogenation of triahalophenols and *p*-halophenols has been recently reported[1]. This feature can be exploited form an analytical point of view.

A carbon-modified electrochemical biosensor for the detection of 2,4,6-trichlorophenol is described. The enzyme chloroperoxidase from *Caldariomyces Fumago* is immobilized on the electrode surface and the dehalogenation product, 2,6-dichloro-1,4-benzoquinone, is electrochemically detected. HPLC and cyclic voltammetry are used to characterize the reaction products and to study the kinetics of the dehalogenation process. Performance characteristics of the sensor: response time, detection limit, linear range, selectivity as well as operating and storage stability are evaluated.

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REFERENCE

1. Osborne R. L., Raner G. M., Hager L. P., Dawson J. H.: J. Am. Chem. Soc. *128*, 1036 (2006).

## PP038

## CATALYSED ELECTROOXIDATION OF SOME CATECHOLS ON PLATINUM MODIFIED WITH FERROCENE DERIVATIVES IMMOBILIZED IN NAFION FILM

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Immobilization of ferrocene and its derivatives into polymer coated electrodes gives the chemically modified electrode that can be used in fundamental electrochemical investigations. The ferrocenes act as effective red-ox mediators for oxidation of organic compounds, such as some phenol and hydroquinone derivatives[1].

The aim of this work was to investigate the electrochemical properties of platinum modified with ethylferrocene and 1,1'-dimethylferrocene immobilized in Nafion film and to determine their electrocatalytic activity in oxidation of some catechols.

The cyclic voltammetry and differential pulse voltammetry were done on such modified electrode (Pt/Nafion/Fc) in aqueous solutions containing catechol, tetrachlorocatechol, guaiacol, 2-chloro-3',4'-dihydroxyacetophenone and 3,4-dihydroxybenzylamine ($10^{-3}$ M each). The results were compared to similar measurements on bare Pt and on bare Pt with these ferrocenes dissolved in solution ($5\times10^{-4}$ M).

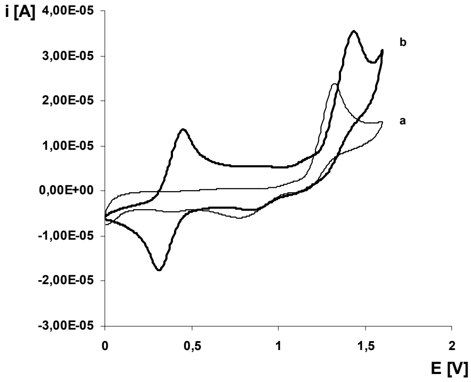

Fig. 1. **Cyclic voltammograms** in 0.1 M $HClO_4$ of: a) guaiacol ($10^{-3}$ M) on Pt, 0.1 V/s; b) guaiacol ($10^{-3}$ M) on Pt/Nafion/Fc, 0.1 V/s; all *vs.* SCE (on AUTOLAB Eco Chemie BV); $T$=298 K

The best results were obtained for modified electrode (Pt/Nafion/Fc). In this case the greater currents of anodic and cathodic peaks of organic compounds oxidation and reduction were obtained which may point to catalytic activity of new conducting phase. The preparative electrolyses in potentiostatic conditions were also done.

REFERENCE

1. Murray R. W., in: *Chemically Modified Electrodes*, *Electroanalytical Chemistry*, Vol. 13, p. 124. Marcel Dekker, New York 1984.

## PP039

## PER-6-THIO-β-CYCLODEXTRIN MODIFIED GOLD ELECTRODES FOR 4,4'-THIODIANILINE DETERMINATION BY SQUARE WAVE VOLTAMMETRY

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Cyclodextrines, well known, are cyclic oligosaccharides whose function like host molecules is well known. The host serves as hydrophilic envelope of the guest and thus increased its the solubility in water and provides additional mechanical, optical and chemical protection.

In this work, the molecule that has beeb employed on the inmobilization of a gold electrode surface was per-6-thio-β-cyclodextrin($S_6CD$) As such, a chemisorbs onto gold surfaces forming at least six S-Au bonds per receptor molecule. Although this derivatization process leads to imperfect monolayers in which a substantial fraction of the gold surface remains uncovered, the monolayers defects can be covered by treatment with a solution of ferrocene and pentanethiol.

Supramolecular host-guest complexes formed between dye molecules, like 4,4'-thiodianinline (TDA), and cyclodextrin molecules are studied with the aim to generate a self-assembled monolayer on a Au surface. The binding of thiolated cyclodextrin to gold surface was studied by induced change in the intensity of the signal generated from the surface.

In the present work, the starting-up of a electrochemical method was developed to determinate TDA by the inmobilization of $S_6CD$ in a gold electrode surface, and the posterior measurement of its electrochemical response through the employment of square wave voltammetry; also have been carried out studies of the formation of inclusion complex with β.cyclidextri. An the posterior application of both molecules in waste water from a textile industry.

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### PP040

## NON-TRADITIONAL ELECTRODE MATERIALS FOR DETECTION OF SUBMICROMOLAR CONCENTRATIONS OF NITRATED EXPOLSIVES

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Detection of low concentrations of nitrated explosives is quite challenging task. Among many analytical methods suitable for this purpose, electroanalytical methods based on easy electrochemical reduction of nitro group, are especially useful for large scale monitoring because of low investment and running costs. The most important task is the development of new electrode materials compatible with field monitoring, with the concept of green analytical chemistry and resistant to passivation which present the biggest problem in practical applications of voltammetric techniques. Using picric acid (2,4,6-trinitrophenol) as a model substance for nitrated explosives, the following non-traditional electrode materials were found promising in this filed. 1. Boron doped diamond thin films (BDDF)[1] which have broad potential window, very low noise and are resistant toward passivation by electrode products[2]. 2. Various forms of solid and paste amalgam electrodes which are environmentally friendly substitutes of mercury electrodes[3]. In this case, problems with passivation can be diminished either by a suitable electrochemical pretreatment or by easy renewal of the electrode surface in the case of amalgam paste electrodes.

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REFERENCES

1. Fujishima A., Einaga Y., Rao T. N., Tryk D. A.: *Diamond Electrochemistry*. Elsevier, Amsterdam 2005.
2. Barek J., Jandová K., Pecková K., Zima J.: Talanta *74*, 421 (2007).
3. Barek J., Fischer J., Navrátil T., Pecková K., Yosypchuk B., Zima J.: Electroanalysis *19*, 2003 (2007).

### PP041

## BIOMIMETIC ENZYME-PROTEIN FILM BY LAYER-BY-LAYER ASSEMBLY: COMMUNICATION IN A PROTEIN STACK

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Communication between proteins in living organisms plays a vital role in many physiological processes. The efficiency and selectivity of signal transfer in natural protein complexes has stimulated interest in constructing artificial signal chains. Protein assemblies with the ability to perform selective signal transduction are of fundamental importance and have application potential in bioelectronics. Implementation of direct electron transfer in protein assemblies was a breakthrough, providing a simple and efficient way for coupling biological recognition events to a signal transducer. An important advance was the fabrication of cyt.c multilayers by electrostatic layer-by-layer self-assembly. With cyt.c and sulfonated polyaniline it was possible that fully electro-active multilayers of the redox protein could be prepared[1]. This approach has recently been extended to design an analytical signal chain based on multilayers of cyt.c and xanthine oxidase (XOD), which relies on an *in situ* generation of a mediating radical and thus allows a signal transfer from hypoxanthine via the substrate converting enzyme and cyt.c to the electrode[2].

Here, we introduce a new type of signal chain by assembling proteins in complexes on electrodes in such a way that a direct protein-protein electron transfer becomes feasible. Our design does not need a redox mediator in analogy to natural protein communication. For this purpose, cyt.c and the enzyme bilirubin oxidase (BOD, EC 1.3.3.5) are co-immobilized in a self-assembled polyelectrolyte multilayer on gold electrodes. The protein architecture facilitates an electron transfer from the electrode via multiple protein layers to molecular oxygen resulting in a significant catalytic reduction current. We anticipate that this concept will stimulate further progress in multilayer design of even more complex biomimetic signal cascades taking advantage of direct communication between proteins.

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REFERENCES

1. Beissenhirtz M. K., Scheller F. W., Stocklein W. F., Kurth D. G., Mohwald H., Lisdat F.: Angew. Chem. Int. Ed. Engl. *43*, 4357 (2004).
2. Dronov R., Kurth D. G., Mohwald H., Scheller F. W., Lisdat F.: Electrochim. Acta *53*, 1107 (2007).

## PP042

## FUNCTIONAL CYTOCHROME C – SULFITE OXIDASE MULTILAYER ASSEMBLY BY PROTEIN-PROTEIN ADSORPTION

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Functional protein multilayer assemblies are of academic interest as simple and flexible model systems for biomimetic signal transfer, and are of practical significance for the design of biosensors and bioelectronic functionalities[1]. Up to date, all the protein multilayers based on electrostatic adsorption reported in literature are stabilized by a polyelectrolyte matrix composed of electrochemically inert polymer[2]. Recently reported assemblies combining cytochrome c (cyt.c) with enzymes and using sulfonated polyaniline (PASA) as a counter polyelectrolyte show high efficiency in electron transfer (ET) throughout the multilayer network[3]. However, avoiding the use of a polyelectrolyte may help to shed more light on the ET mechanism within multiprotein arrangements.

Here we introduce a novel strategy for multi-protein layer-by-layer (LbL) assembly combining the redox protein cyt.*c* with the enzyme sulfite oxidase (SOx) without use of any additional polymer. QCM confirmed mass accumulation at the surface with each deposition cycle. The assembly is carried out by alternating co-adsorption of SOx and cyt.*c*. Electrostatic interactions between these two proteins with rather separated isoelectric points during the assembly process from a low ionic strength buffer were found to be sufficient for LbL deposition of the both proteins. This arrangement shows ability to transport electrons from the substrate in solution to the electrode over longer distances, thus, supporting the idea of direct inter-protein electron exchange as a principle ET mechanism. The electrodes show catalytic activity towards sulfite oxidation, proportional to the number of the deposited layers. The design does not require the use neither of additional redox mediators, nor a synthetic polymer as a polyelectrolyte, which makes this approach interesting for the construction of third generation biosensors.

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REFERENCES

1. Willner I., Katz E.: Angew. Chem., Int. Ed. Engl. *39*, 1180 (2000).
2. Jessel N.: Adv. Mater *15*, 692 (2003).
3. Beissenhirtz M. K.: Angew. Chem. Int. Ed. Engl. *43*, 4357 (2004).

## PP043

## THERMAL BEHAVIOUR OF HEATED ELECTRODES

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In the recent years investigations at electrically heated electrodes became more and more convenient[1]. The main approach in this development can be seen in the use of inductor bridges as presented shortly[2]. By using this filtering element, the heating current (AC between 50 and 100 kHz, and ca. 1 A) can be separated from the electrochemical signal (1 nA to 10 μA) which leads to nice signals without any major disturbances. So the construction of very symmetrical electrodes with three contacts is no more necessary. Also the production of compact and versatile instruments for radio frequency heating and their application to electrochemical measurements have been reported[3]. Nevertheless with the mostly used electrodes (metal wires) you still have the problem of a temperature gradient at the electrode surface due to different heat spreading situations in the middle or at the end of an electrode. To determine the amount of this effect we performed numerical simulations. In contrary to electrochemical experiments which usually provide you with information only about the average temperature of the surface, mathematical simulations give you information about each point of the electrode surface. As could be assumed, it was evaluated that there is a temperature gradient at the electrode.

In a second step we tried to minimize this gradient by using different shapes for the electrode. With a specially designed electrode, a homogeneous temperature could be achieved as proved by the simulations.

To investigate the amount of heat being transferred into a solution, we made some experiments with a completely new designed 16-electrode array. Each of the electrodes can be heated individually or used as a temperature sensor. This makes it possible to get some experimentally proved information about heat allocation in the solution.

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REFERENCES

1. www.hot-wire-electrochemistry.com
2. Flechsig G.-U., Gimsa J., Gründler P., Grabow H.: DE-Patent 10 2006 006 347 B3, PCT Int. Appl (2007).
3. Wachholz F., Gimsa J., Duwensee H., Grabow H., Gründler P., Flechsig G.-U.: Electroanalysis *19*, 535 (2007).

## PP044
## THE STRIPPING VOLTAMMETRIC DETERMINATION OF MERCURY IN AIR WITH A CHROMATOMEMBRANE PRECONCENTRATION

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The capability of determination of mercury in air by stripping voltammetry with chromatomembrane preconcentration was studied. The limit of detection of mercury in an absorbing solution was $2.5\times10^{-11}$ M.

The capability of separation of mercury in air and previous determination by stripping voltammetry was design. The mercury from air in discrete regime of the chromatomembrane process was separated. Thereto, inlet and outlet of aqueous phase are recovered clamps and let pass through cell outsider the microporous membrane a blast with weight hour space velocity 0,01 l min$^{-1}$ during stated interval time. After stopped gas flow absorbate eluated with absorption mercury from chromatomembrane cell by solution for absorbed of mercury. Absorbate with mercury was analyzed in the voltammetric analyzer.

As a received results of experiments different the liner dependence concentration of mercury (1–15 μg l$^{-1}$) by using various against the time of flow of air sample was obtained. For comparison received results and for calculate of coefficient of concentration dependence quantity of mercury against the volume of air sample for measures with chromatomembrane cell and bubble absorbers was obtained. From the results obtained in this study the coefficient of concentration was calculated.

Flow of air sample with mercury let pass through chromatomembrane cell and two bubble absorbers for completeness absorption extraction and analyzed.

These results indicates that the quantitative absorption efficiently of mercury with chromatomembrane absorption.

## PP045
## THE RAPIDE STANDARTLESS STRIPPING VOLTAMMETRY TECHNIQUE FOR DETERMINATION HEAVY METAL IONS IN AQUEOUS SOLUTIONS

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A rapide standartless stripping voltammetry method for heavy metal ions determination in aqueous solutions was proposed. The application of the method was checked up on the determination of mercury, cadmium, copper and lead.

Recently, standartless combined electrochemical method was proposed. It is based on the carrying out stripping voltammetry measurements and following quantity of electricity ($Q_\infty$) calculation from the Meites formula, which corresponds to complete metal deposition. The main limitation of the method is the necessity of carrying out at least three measurements and that increases the time of analysis considerably.

The rapid standartless method is based on the determination of coulometric constant $k$ for given cell and following quantity of electricity calculation from the formula:

$$Q_\infty = \frac{Q_\mathrm{t}}{1 - e^{-k\cdot t_{\mathrm{depэ}}}}$$

where $Q_\mathrm{t}$ is the quantity of electricity that was spend on the deposition of substance by the time $t_\mathrm{dep}$, $k$ is the coulometric constant of the cell.

Coulometric constant was experimentally found from the plots of dependences, shown by following equation:

$$\lg(C_i/C_0) = -k\cdot t_{\mathrm{dep.}}$$

where $C_\mathrm{i}$ is the value of concentration of the studied solution after electrolysis time $t_\mathrm{e}$, $C_0$ is the first concentration. $C_\mathrm{i}/C_0$ ratio was found by consecutive electrolytic extraction of metal from the small volume solutions (1–5 ml).

The dependence of coulometric constant on the volume of the studied solution was analysed for gold and gold-film electrodes in case of determination of mercury and mercury-film electrode in case of determination of lead.

Experimental check of the method was carried on the modeling solutions in the concentration range $1.10^{-8}$ – $1.10^{-7}$ mol L$^{-1}$ (for mercury, cadmium, copper and lead) by method standard addition. The obtained concentration values have a good correlation with predetermined concentration.

## PP046

## AUTOMATED ANALYSIS OF PROTEINS USING BRDICKA REACTION

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Protein detection based on Brdicka reaction was discovered by Rudolf Brdicka in the forties of 20th century. It is based on determination of the catalytic evolution of hydrogen in the presence of heavy metal complex. According to Brdicka findings we use ammonia buffer (pH 9) with 1 mM $[Co(NH_3)_6]Cl_3$ as supporting electrolyte. The advantages of this method are rapidity, sensitivity and low cost. However the main drawback of this method is necessity of the manual control of injection of a sample. Therefore we had looked for the possibility to automate the measurements. To automate measurements 747 VA Stand instrument connected to 746 VA Trace Analyzer and 695 Autosampler with cooled sample holder was employed. A measurement proceeds as follows: A sample is positioned on the thermostatic sample holder (4 °C). The electrochemical cell with three electrodes (working electrode – hanging mercury drop electrode, referent electrode – Ag/AgCl/3M KCl electrode, auxiliary electrode – platinum electrode) is rinsed with distilled water (3×25 ml MiliQ water) using three computer controlled pumps. After draining of the water the supporting electrolyte (temperature 4 °C) is pipetted into the washed cell. Further a sample is introduced using the autosampler. The syringe from the autosampler is rinsed and the sample is injected to the cell. The measurement itself consists of a few following processes: At first, the injected sample is accumulated on the surface of hanging mercury drop electrode at open circuit for two minutes. At second, the current responses as function of various potentials are measured. At third, the measured values are processed by 746 VA Trace Analyser and transferred to a personal computer. At fourth, the transferred data is then processed using GPES 4.9 software. The instruments were successfully tested on determination of protein called metallothionein, which could be considered as a new tumour disease marker.

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REFERENCES

1. Brdicka R.: Nature *139*, 330 (1937).
2. Petrlova J., Potesil D., Mikelova R., Blastik O., Adam V., Trnkova L., Jelen F., Prusa R., Kukacka J., Kizek R.: Electrochim. Acta *51*, 5112 (2006).

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## PP047

## DETERMINATION OF LEAD AND CADMIUM BY SQUARE-WAVE ANODIC STRIPPING VOLTAMMETRY AT DIGITAL VERSATILE DISC-BASED Ag ELECTRODES

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Due to the increased concern of hazardous effects of lead and cadmium, there is an increasing interest in the developments of methods for the determination of lead and cadmium[1–7]. Electrochemical techniques are very attractive because of its low cost, easy operation, good sensitivity, and high speed. For electrochemical techniques, the selection of electrode material is important. Because of their high sensitivity and remarkable reproducibility, mercury-based electrodes are widely employed for the determination of lead and cadmium[1,4]. However, mercury is very toxic. And mercury-based electrodes are now being progressively replaced by other electrodes[5–25], such as bismuth-based electrodes[5–16], glassy-carbon electrodes[17], iridium electrodes[18], and silver electrode[19–25].

Compact disks (CD) are generally constructed from five layers of material, including a polycarbonate base, an organic dye layer, a nanometric metal reflective layer, a protective polymer film, and a data shield. During the last few years, CD has been used as interesting electrode materials for various electrochemical studies[26–32]. Digital Versatile disc (DVD) is considered to be a CD future replacement.

In this study, we report a new method to construct electrodes from DVD. Since silver electrode are frequently used for simultaneous determination of $Pb^{2+}$ and $Cd^{2+}$ we used DVD-based silver electrode here for square-wave anodic stripping voltammetry analysis of $Pb^{2+}$ and $Cd^{2+}$. The effect of $I^-$ on the stripping analysis of $Pb^{2+}$ and $Cd^{2+}$ at silver electrodes was first studied. The addition of $I^-$ improved the shape and current of the stripping peaks of both $Pb^{2+}$ and $Cd^{2+}$, allowing success determination of $Pb^{2+}$ and $Cd^{2+}$ at DVD-based silver electrodes.

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REFERENCES

1. Wang J., in: *Stripping Analysis: Principles, Instrumentation and Applications.* VCH Publishers, Deerfield Beach 1985.
2. Banks C. E., Compton R. G.: Electroanalysis *15*, 329 (2003).
3. Economou A., Fielden P. R.: Analyst *128*, 205 (2003).
4. Mikkelsen O., Schroder K. H.: Electroanalysis *15*, 679 (2003).

5. Wang J., Lu J., Hocevar S. B., Farias P. A. M., Ogorevc B., Farias P. A. M.: Anal. Chem. *72*, 3218 (2000).
6. Wang J.: Electroanalysis *17*, 1341 (2005).
7. Economou A.: TRAC-Trend Anal. Chem. *24*, 334 (2005).
8. Wang J., Lu J., Hocevar S. B., Ogorevc B.: Electroanalysis *13*, 13 (2001).
9. Pauliukaite R., Brett C. M. A.: Electroanalysis *17*, 1354 (2005).
10. Kachoosangi R. T., Banks C. E., Ji X. B., Compton R. G.: Anal. Sci. *23*, 283 (2007).
11. Banks C. E., Kruusma J., Hyde M. E., Salimi A., Compton R. G.: Anal. Bioanal. Chem. *379*, 277 (2004).
12. Kruusma J., Banks C. E., Compton R. G.: Anal. Bioanal. Chem. *379*, 700 (2004).
13. Gouveia-Caridade C., Pauliukaite R., Brett C. M. A.: Electroanalysis *18*, 854 (2006).
14. Svancara I., Baldrianova L., Tesarova E., Hocevar S. B., Elsuccary S. A. A., Economou A., Sotiropoulos S., Ogorevc B., Vytras K.: Electroanalysis *18*, 177 (2006).
15. Krolicka A., Pauliukaite R., Evancara I., Metelka R., Bobrowski A., Norkus E., Kalcher K., Vytras K.: Electrochem. Commun. *4*, 193 (2002).
16. Baldrianova L., Svancara I., Economou A., Sotiropoulos S.: Anal. Chim. Acta *580*, 24 (2006).
17. van Staden J. F., Matoetoe M. C.: Anal. Chim. Acta *411*, 201 (2000).
18. Nolan M. A., Kounaves S. P.: Anal. Chem. *71*, 3567 (1999).
19. Bonfil Y., Brand M., Kirowa-Eisner E.: Anal. Chim. Acta *464*, 99 (2002).
20. Brand M., Eshkenazi I., Kirowa-Eisner E.: Anal. Chem. *69*, 4660 (1997).
21. Zen J. M., Yang C. C., Kumar A. S.: Anal. Chim. Acta *464*, 229 (2002).
22. Bonfil Y., Kirowa-Eisner E.: Anal. Chim. Acta *457*, 285 (2002).
23. Mikkellse O., Schroder K. H.: Electroanalysis *13*, 687 (2001).
24. Bagel O., Lagger G., Girault H. H., Brack D., Loyall U., Schafer H.: Electroanalysis *13*, 100 (2000).
25. Zen J. M., Yang C. C., Kumar A. S.: Electrochim. Acta *47*, 899 (2001).
26. Angnes L., Richter E. M., Augelli M. A., Kume G. H.: Anal. Chem. *72*, 5503 (2000).
27. Richter E. M., Augelli M. A., Magarotto S., Angnes L.: Electroanalysis *13*, 760 (2001).
28. Yu H. Z.: Chem. Commun. *2004*, 2633.
29. Daniel D., Gutz I. G. R.: Electrochem. Commun. *5*, 782 (2003).
30. Westbroek P., De Strycker J., Dubruel P., Temmerman E., Schacht E. H.: Anal. Chem. *74*, 915 (2002).
31. Richter E. M., de Jesus D. P., Neves C. A., do Lago C. L., Angnes L.: Quim. Nova *26*, 839 (2003).
32. Daniel D., Gutz I. G. R.: Electroanalysis *13*, 681 (2001).

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## PP048

# CARBON NANOTUBES MODIFIED DNA BIOSENSORS FOR THE DETECTION OF DAMAGE TO DNA CAUSED BY LIPID OXIDATION PRODUCTS

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Lipid peroxidation is a critically important reaction in physiological and toxicological processes as well as in food products[1]. The main products of this reaction are hydroperoxides and decomposition of hydroperoxides leads to formation of mixture of secondary lipid peroxidation products involving aldehydes, mostly malondialdehyde (MDA). Both hydroperoxides and MDA are mutagenic and genotoxic. Hydroperoxides generate free radicals by reaction with the transition metal ion complexes in Fenton-like reaction:

$$ML_m^{\,n} + H_2O_2 \rightarrow ML_m^{\,n+1} + \bullet OH + OH^-$$

where M is low valent transition metal ion, L is any ligand complexed to metal, n refers to the charge on the metal ion. Free radicals formed in this reaction can attact the DNA and cause its damaging and mutations. Malondialdehyde reacts with DNA and form MDA-deoxyguanosine adducts[2] wich have mutagenic properties.

DNA biosensors are used advantageously to study the damage to DNA[3,4] as well as possibility of DNA protection by antioxidants[5]. In recent years, different nanomaterials are used to enhance the detection properties of DNA biosensors.

In our work we modified commertial screen-printed carbon electrodes with multi-walled carbon nanotubes (MWNT) or single-walled carbon nanotubes (SWNT) and double-stranded calf thymus DNA (dsDNA) to prepare the nanostructured DNA biosensors. Cyclic voltammetry of $K_3[Fe(CN)_6]$, square-wave of $[Ru(bpy)_3]^{2+}$ and electrochemical impedance spectroscopy were used to evaluated the properties of the biosensors.

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REFERENCES

1. Termini J.: Mutat. Res. *450*, 107 (2000).
2. Marnett J. L.: Mutat. Res. *424*, 83 (1999).
3. Vaníčková M., Lehotay J., Čižmárik J., Labuda J.: Bioelectrochem. *66*, 125 (2005).
4. Ferancová A., Bučková M., Korgová E., Korbut O., Grundler P., Warnmark I., Štěpán R., Barek J., Zima J. Labuda J.: Bioelectrochem. *67*, 191 (2005).
5. Ferancová A., Heilerová L., Korgová E., Šilhár S., Štěpánek I., Labuda J.: Eur. Food Res. Technol. *219*, 416 (2004).

## PP049

## DIRECT ELECTRON TRANSFER BASED GLUCOSE OXIDASE BIOSENSORS

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One of the main problems affecting the development of first generation electrochemical biosensors for the analysis of real matrices is the interference of electroactive species eventually present in the sample under investigation. To solve this problem several approaches have been followed: among them third generation biosensors based on direct electron transfer (DET) display the most interesting features to this end. In this work we have realized and fully characterized several DET-biosensors based on glucose oxidase (GOx) for glucose analysis. All of them use the horseradish peroxidase (HRP) as redox mediator to assure the electrochemical communication between GOx and electrode surface. The HRP was immobilized onto the electrode surface using different immobilization procedures: *i*) polyazetidine prepolymer; *ii*) scleroglucan/borax gel; *iii*) reticulated anion exchange resin (Tri-butyl-methyl-phosphonium polystyrene reticulated with 1.1% di-vinyl-benzene). GOx was immobilized onto the resulting HRP-electrodes. Results obtained are discussed herein showing that a more wide range of biosensors is obtained thus enabling to optimize the glucose biosensor performances in view of a more selective determination of glucose in real samples.

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## PP050

## ELECTROENZYMATIC REACTIONS WITH GatDH, GatDH-Cys AND P2OxB1H ON POLY- AND NANOCRYSTALLINE GOLD AND PLATINUM ELECTRODES

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A complete biocatalytic chain is realized on gold electrodes by immobilisation of the redox mediator CTFM, the cofactor NADH and the native enzyme galactitol dehydrogenase (GatDH). The fixation of all components on the electrode surface is conducted by a Nafion® coating. The electrochemical oxidation of the enzymatically reduced cofactor NADH is observed by cyclic voltammetry. The electrochemical regeneration of NADH represents an alternative to the classical enzymatical recycling and could allow the preparation of enantiomerically pure fine chemicals. By means of nanocrystalline gold the electrochemically active surface area und thus the reaction rate is increased by a factor of 15 compared to coarse-grained gold. In addition the electrochemical regeneration of the cofactor is inverstigated using a cysteine-modified GatDH (GatDH-Cys). This enzyme is directly immobilized on the gold electrode via the formation of thiole bonds whereas the mediator in this case is in solution. One advantage is the directed immobilisation of the enzyme without a prior surface functionalization, e.g. with a SAM.

Electroenzymatics without external cofactor is performed with pyranose-2-oxidase (P2OxB1H) immobilized on nanocrystalline platinum electrodes by electropolymerisation of tyramine. The enzyme catalyzes the regioselective oxidation of many polyhydroxyaldehydes to the corresponding ketoaldoses in the presence of oxygen. Simultaneously hydrogen peroxide is formed, which can be removed by electrochemical reoxidation to oxygen. This step is monitored by means of chronoamperometry at +600 mV *vs.* Ag/AgCl; the evaluation of these data in terms of the Michaelis-Menten kinetics yields the intrinsic enzymatic activity.

## PP051

## POLYETHYLENEIMINE-CARBON NANOTUBES COMPOSITE MODIFIED ELECTRODES FOR DNA-QUINAZOLINES INTERACTION STUDY

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In the present work, electrochemical DNA biosensor is proposed as a monitoring device for the rapid bio-analysis of DNA-drug interaction studies. In experiment modified screen-printed carbon electrodes (SPCE) were used. The working electrode was modified by using multi-walled carbon nanotubes (MWNT) dispersed in polyethylenimine (PEI)[1]. The binding of different molecules to DNA immobilized on disposable screen-printed electrodes has been measured through a variation of the electrochemical signal of guanine by square wave voltammetric (SWV) scans using $[Ru(bpy)_3]^{2+}$ as the indicator, by cyclic voltammetry (CV) with the $K_3[Fe(CN)_6]$ indicator and electrochemical impedance spectroscopy (EIS). In this way, the DNA-s interactions are supposed to be studied for two quinazoline derivatives having potential anticancer activity[2].

EIS is known as a powerful tool for the electrode surface characterization by means of changes in resistance, capacitance and surface roughness. The impedance spectra have shown a difference in the resistance properties of the DNA layer after long time incubation in quinazolines in solution and thus supported the fact of their biological activity towards DNA. The CV results have shown a decrease in the peak potential separation for the $K_3[Fe(CN)_6]$ redox probe with increased concentration of quinazolines. The incubation longer than 1 hour acccelerates, as expected, this decrease. The electron transfer between electrode surface and solution is simplified via changes in the DNA layer after interaction with such a complex structure. The SWV scans have shown additive adsorption of quinazolines, mainly at it's concentration higher than 50 μg ml$^{-1}$. The SWV current response before and after incubation in quinazolines at various concentrations was examined.

Utilization of this sensor represents a rapid and simple method for potential drugs testing.

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REFERENCES

1. Rubianes M. D., Rivas G. A.: Electrochem. Commun. *9*, 480 (2007).
2. Ovádeková R., Jantová S., Labuda J.: Anal. Lett. *15*, 2625 (2005).

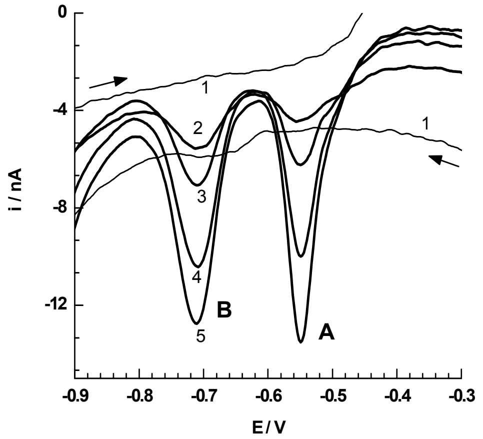

Fig. **CSV of HCy and Ni$^{2+}$ containing solutions**. HCy (μM): (1) 0; (2) 0.6; (3) 1.0; (4) 1.4; (5) 1.8. Supporting electrolyte: 0.05 M $Na_2HPO_4$ and 4 mM Ni$^{2+}$, pH 6.5, *E*(dep): +0.1 V, *t*(dep): 30 s, 50 mV s$^{-1}$, HMDE

## PP052

## CATHODIC STRIPPING VOLTAMMETRY OF HOMOCYSTEINE AND THE RESPECTIVE THIOLACTONE AT A MERCURY ELECTRODE

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Homocysteine (HCy) causes vascular disease by a direct effect on arterial cells and tissues[1,2]. Elevation of blood HCy concentrations is a result of dietary, genetic, metabolic, hormonal, or toxic factors. Because of its similarity to the protein amino acid methionine, HCy can enter the protein biosynthetic pathway. However, HCy cannot complete the protein biosynthetic process and is converted to HCy-thiolactone (HTL,) by a reaction catalyzed by methionyl-transfer RNA synthetase[3,4]. Accumulating evidence suggests that HTL plays an important role in atherogenesis and thrombosis[5]. As far as the electrochemical behavior is concerned, owing to the analogy of chemical structure, HCy behave in many respects like cysteine (Cys), although some difference have been noticed mostly in connection with the metal ion chelate formation[6].

Under anodic polarization at a mercury electrode, homo-cysteine (HCy) forms a sparingly soluble mercury thiolate and mercury ion reduction in this compound gives rise to a characteristic cathodic stripping peak (A). If the nickel ion is present, HCy released by this reaction does catalyze nickel ion reduction, yielding a second cathodic peak (B) at about –0.75 V (Fig. 1). Regarding peak A, nickel ion has no effect upon this response. Homocysteine-thiolactone (HTL) is electrochemically inactive under similar conditions, but HCy impurity present in the commercial MTH reagent develops both peaks A and B under suitable conditions. HCy impurity in HTL can therefore be assessed in experiments performed in the cathodic stripping voltammetric mode.

It can be concluded that, as found, HTL is electrochemically inactive under the conditions of CSV at a mercury electrode, either in the absence or in the presence of Ni$^{2+}$ ion. However, HCy which is present as an impurity at the level of about 3 % undergoes characteristic electrochemical reactions occurring in a HTL solution and, due to mercury ion reduction in the mercury thiolate, the choice of CSV thus enables the determination of HCy in HTL samples.

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REFERENCES

1. McCully K. S.: Am. J. Clin. Nutr. *86*, 1563S (2007).
2. Přistoupilová K., Přistoupil T. I., Heyrovský M.: Chem. Listy *93*, 365 (1999).
3. Jakubowski H.: Cell. Mol. Life Sci. *61*, 470 (2004).
4. Jakubowski H., Zhang L., Bardeguez A., Aviv A.: Circ. Res. *87*, 45 (2000).
5. Jakubowski H.: Clin. Chem. Lab. Med. *45*, 1704 (2007).
6. M. Heyrovský, S. Vavřička: Bioelectrochem. Bioenerg. *48*, 43 (1999).
7. Galík M., Banica A., Vytřas K., Švancara I., Banica F. G., in: *Sensing in Electroanalysis*, Vol. 2 (Vytřas K., Kalcher K., ed.), p. 95–103. University of Pardubice, Pardubice 2007.
8. Spataru N., Banica F. G.: Analyst *126*, 1907 (2001).

## PP053

## USING THIOUREA AS SOURCE FOR ELECTROCHEMICAL GENERATION OF METAL SULFIDES

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Metal sulfide chemistry is a topic of particular interest for geochemistry and environmental chemistry. However, manipulation of the sulfide ion is not a straightforward task due to its volatility at pH<12, interaction with metal ion impurities, easy oxidation and formation of polysulfides. We describe here a method for electrochemical investigation of metal sulfides that makes use of a stable sulfur derivate (like thiourea, TU) in order to prepare a layer of metal sulfide by the anodic reaction of the electrode metal. Other metal sulfides can be prepared by exchange reaction with the metal ion of interest. This procedure was inspired by analogous investigation using sulfide ion as starting material[1].

Anodic reaction of TU at a mercury electrode results in an HgS surface layer. Mercury reduction in this compound occurs in a good agreement with the model that assumes a reversible electron transfer reaction and a constant activity of the surface compound[1,2]. If a metal ion is present in the solution phase, $Hg^{2+}$ is released by an exchange reaction and the cathodic peak gets shifted to less cathodic potentials.

It is possible therefore to prepare metal sulfides using a stable sulfur derivative as a starting material. Metal sulfides prepared in this way are amenable to electrochemical investigations. This method can easily be transposed to metal selenides investigation if an organic selenium derivative (like selenourea) is used as starting material. It would also be of interest to perform such investigations using silver as electrode in order to prepare and study silver chalcogenides. On the other hand, the matter here presented is of relevance for research of metal sulfides in natural waters. A proposed method for investigating soluble metal ion complexes with the hydrogen-sulfide anion is based on square-wave cathodic stripping voltammetry of sulfide ion in the presence of the metal of interest[7]. In the frame of this method, the DeFord and Hume approach was employed to infer the composition and stability of the complexes from the shift of the peak potential in the presence of the metal ion. Severe faults of this method were already emphasized[8, 9]. Data in Ref. 1, as well as the results in this paper point out an additional drawback of the method in Ref.7, namely the omission of the exchange of $Hg^{2+}$ in HgS with the metal ion in the solution. The exchange reaction renders the DeFord and Hume approach not suitable under these circumstances.

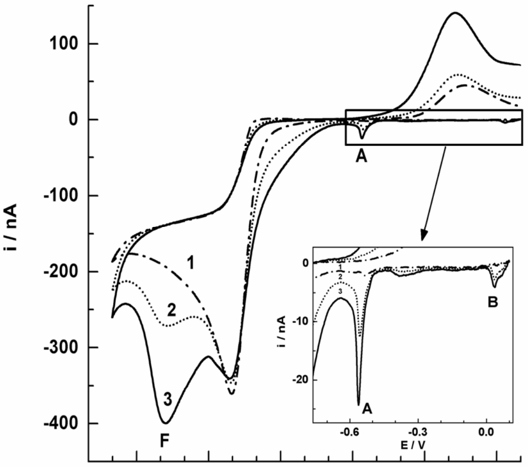

Fig. **Electrochemical reactions in the presence of $Ni^{2+}$ after anodic polarization at +0.1 V in the presence of TU**. Phosphate buffer, pH 6.5; $2.10^{-7}$ M TU; $4.10^{-4}$ M $Ni^{2+}$; $t_d$ (s): (1) 0; (2) 30; (3) 60

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REFERENCES

1. Corney J. H., Laitinen H. A.: Anal. Chem. 42, *473* (1970).
2. Berzins T., Delahay P.: J. Am. Chem. Soc. *75*, 555 (1953).
3. Nicholson M. M.: J. Am. Chem. Soc. *79*, 7 (1957).
4. Banica F. G., Spataru N., Spataru T.: Electroanalysis *9*, 1341 (1997).
5. Spataru N., Banica F. G: Analyst *126*, 1907 (2001).
6. Banica F. G., Spataru N.: Talanta *44*, 491 (1999).
7. Luther G. W., III, Rickard D. T., Theberge S., Olroyd A.: Environ. Sci. Technol. *30*, 671 (1996).
8. Davisson W.: Environ. Sci. Technol. *30*, 3638 (1996).
9. Banica F. G., Ion A.: Talanta *45*, 1031 (1998).

## PP054

## A NEW POLYMERIC PHENOTHIAZINE COMPOUND FOR ELECTROCATALYTIC OXIDATION OF NADH

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Azines type dyes such as phenazines, phenothiazines and phenoxazines, which undergo a reversible 2 electron-proton reduction to yield their corresponding leuco forms, have often been used as redox mediators for electrocatalytic oxidation of NADH, since they exhibit great electrocatalytic activity toward NADH oxidation. These mediators are usually immobilized on the electrode surface by covalent attachment[1], adsorption[2], electropolymerization[3] or by entrapment within carbon paste modified supporting material such as layered compounds (e. g. zeolite, zirconium phosphate, titanium phosphate etc.)[4,5].

In this work, a new polymeric phenothiazine compound, poly-phenothiazine formaldehyde (PPF) was used as redox mediator for electrocatalytic oxidation of NADH. In order to prepare chemically modified electrodes with PPF, the phenothiazine derivative was immobilized onto the surface of a graphite electrode *via* adsorption, from a dimethylsulfoxide solution.

The results showed that the proposed modified electrodes could be used for electrocatalytic oxidation of NADH in phosphate buffer (pH 7.0) with an overpotential of less than 400 mV compared with that of bare electrodes. It is worth to mention, that when the surface of the modified electrode was irradiated with a light source (250 W Halogen lamp), the electrocatalytic oxidation current of NADH was increased with about 1.7 times compared with the absence of irradiation. The second order electrocatalytic rate constant ($k_{\mathrm{obs},\,[\mathrm{NADH}]=0}$) was calculated from rotating disk electrode experiments at various concentrations of NADH and phosphate buffer with different pH values and good values (3879.3 $M^{-1} s^{-1}$ at pH 7.0) were obtained.

REFERENCES

1. De Lucca A. R., Santos A. S., Pereira A. C., Kubota L. T.: J. Colloid Interface Sci. *254*, 113 (2002).
2. Dicu D., Muresan L., Popescu I. C., Cristea C., Silberg I. A., Brouant P.: Electrochim. Acta *45*, 3951 (2000).
3. Karyakin A. A., Karyakina E. E., Schmidt H.-L.: Electroanalysis *11*, 149 (1999).
4. Dicu D., Munteanu F. D., Popescu I. C., Gorton L.: Anal. Lett. *36*, 1755 (2003).
5. Gligor D., Muresan L. M., Dumitru A., Popescu I. C.: J. Appl. Electrochem. *37*, 261 (2007).

## PP055

## VOLTAMMETRIC ELECTROSYNTHESIS OF MOLECULARLY IMPRINTED POLYMERS IN SEMIORGANIC MEDIA. DINITRO-*o*-CRESOL AS CASE OF STUDY AND DESIGN OF A SELECTIVE MICROSENSOR

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Molecularly imprinted materials are becoming one of the most promising techniques for the selective determination of analytes in electrochemistry, particularly in the modification of the surface of electrodes with the aim of generating selective cavities to the target analyte[1]. In spite of the fact that their use has been widely expanded in extraction techniques[2] or in chromatography[3], MIP modified sensors remains still as one of the most promising field among the multiple applications of molecularly imprinted materials.

Most of MIP based sensors have been synthesized by radical polymerization employing acrylic or vinylic type of monomers[4], however, in the last years, different polymerization techniques are gaining interest such as electrosynthesis. This technique allows the generation of a compact and rigid polymeric matrix which is very suitable for the generation of molecular prints. Most of the works related to electrosynthesized MIP, are referred to MIP sensors synthesized in aqueous media[5]. However, these procedures are limited to water soluble compounds. This fact is a disadvantage when low polarity analytes want to be determined. In order to solve this problem, an analytical methodology for the electrosynthesis of MIP is proposed with the objective of determining selectively dinitrophenolic pesticides such as dinitro-*o*-cresol or DNOC.

The MIP based sensor was synthesized potentiodinamically by cyclic voltammetry employing the monomers aniline and *o*-phenylenediamine in a methanol containing medium (50 %). The polymeric film obtained this way was rigid and compact and showed high stability. To generate imprinted sites on the polymeric surface, DNOC was also added to the polymerization mixture in a concentration of 9 mM. The so obtained sensor was able to recognize the target analyte giving a sensitivity of $1.64 \times 10^3$ nA $M^{-1}$ with good repeatability <8 %.

With the aim of testing the selectivity of the sensor, the analytical signal of the target analyte was evaluated against other dinitrophenolic compounds. It could be seen that it existed a remarkable peak intensity difference when the signal corresponding to the DNOC and the signal corresponding to non-specific compounds were compared.

REFERENCES

1. Blanco-Lopez M. C., Gutierrez-Fernandez S., Lobo-Castanon M. J., Miranda-Ordieres A. J., Tunon-Blanco P.: Anal. Bioanal. Chem. *378*, 1922 (2004).
2. Tamayo F. G., Turiel E., Martin-Esteban A.: J. Chromatogr., A *1152*, 32 (2007).
3. Haginaka J.: Trends Chromatogr. *1*, 111 (2005).
4. Blanco-Lopez M. C., Lobo-Castanon M. J., Miranda-Ordieres A. J., Tunon-Blanco P.: TrAC, Trends Anal. Chem. *23*, 36 (2004).
5. Liu K., Wei W.-Z., Zeng J.-X., Liu X.-Y., Gao Y.-P.: Anal. Bioanal. Chem. *385*, 724 (2006).

## PP056

## DIFFERENT CNTs-FUNCTIONALIZED GOLD SPEs MODIFICATION: APPLICATION FOR GENOSENSORS TRANSDUCTORS

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One of the more relevant trends in Science in general and in Analytical Chemistry in particular is the use of nanotechnology. The use and application of nanostructured materials, a bottom-up approach of miniaturisation, is in continuous increase.

In this context, the combined use of screen-printed electrodes[1], manufactured employing thick-film technology, and carbon nanotubes results extremely advantageous for the Electroanalytical field. A considerable enhancement of the sensitivity as well as the favourable kinetic of electronic transfer, low response times and the possibility of working with low-conductivity media are very promising.

The objective of this work is then, the electrochemical characterisation of CNT-modified gold-SPEs. CNTs[2] have been employed in combination with carbon-SPEs but their use with gold-SPEs is new. It is known the relevance of the surface in the performance of the electrode.

In order to know if the functionalisation of CNTs is of relevance, three different CNTs: –COOH, –SH and $-NH_2$ functionalised have been employed. They have been dispersed in several media and the electrochemical behaviour has been checked by cyclic voltammetry, differential pulse voltammetry and square wave voltammetry.

As the final objective of the work is the construction of a promising genosensor on the modified gold surface, an electroactive label has been the chosen analyte. Methylene blue, an electroactive organic dye, has been employed in this work since it gives an adequate electrochemical signal[3] and can be covalently attached to DNA-strands.

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REFERENCES

1. García-González R., Fernández-Abedul M. T., Costa-García A.: Electrochim. Acta *53*, 3242 (2008).
2. Fernández-Abedul M. T., Costa-García A.: Anal. Bioanal. Chem. *390*, 293 (2008).
3. Castaño-Álvarez M., Fernández-Abedul, Costa-García A.: Electrophoresis *28*, 4679 (2007).

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## PP057

## Cu(II) DETECTION AT CARBON PASTE ELECTRODES MODIFIED WITH CYCLAM-FUNCTIONALIZED MESOPOROUS SILICA MATERIALS

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Silica-based organic-inorganic materials combine the advantages of an inorganic backbone (mechanical stability, high porosity and possible control of pore size and 3D pore arrangement) and the chemical reactivity of organic groups[1]. Both organic and inorganic properties have strong influence on the adsorption of heavy metals in aqueous solution. Modifying electrodes with such materials can lead to an improvement of the sensitivity and selectivity of the sensor due to the preconcentration of the target analytes at open-circuit prior to their electrochemical detection by anodic stripping voltammetry[2,3].

Among organo-functional groups, those belonging to the family of polyazamacrocycles, i.e. cyclam, display very interesting properties for sensing applications. Indeed, they form stable complexes with a large number of transition metal ions and their complexing properties can be tuned by a judicious choice of the organic groups attached to the macrocycle.

In the present work, cyclam moieties have been grafted onto the surface of silica materials displaying ordered (SBA15) or amorphous (K60) mesoporosity. Both hybrid materials have been dispersed in carbon paste and the resulting modified electrodes have been successfully exploited for voltammetric detection of Cu(II). The strong binding properties of cyclam towards Cu(II) species are kept when bound to silica and cyclam-functionalized silica acts as a powerful preconcentration agent. Surprisingly, a well-ordered silica does not improve significantly the electrode response, suggesting that the accumulation process may be restricted by chemical reactivity of immobilized cyclam towards Cu(II), rather than diffusion of the analyte into the silica network. The influence of interfering species (Co(II), Ni(II), Cr(III)…) on the electrochemical detection of Cu(II) and the analytical characteristics of the sensor have been studied.

REFERENCES

1. Walcarius A.: Chem. Mater. *13*, 3351 (2001).
2. Walcarius A., Etienne M., Sayen S., Lebeau B.: Electroanalysis *15*, 414 (2003).
3. Etienne M., Bessière J., Walcarius A.: Sens. Actuators, B *76*, 531 (2001).
4. Denat F., Brandès S., Guilard R.: Synlett *5*, 561 (2000).
5. Meyer M., Dahaoui-Gindrey V., Lecomte C., Guilard R.: Coord. Chem. Rev. *178*, 1313 (1998).

## PP058

# ELECTROCHEMICAL ANALYSIS OF THE KINETICS OF NITRIC OXIDE RELEASE FROM TWO DIAZENIUMDIOLATES IN BUFFERED AQUEOUS SOLUTION

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To better understand the biological role and effects of NO, several types of NO-donor molecules with different physico-chemical properties and reactivity have been synthesized to study its *in vitro* and *in vivo* endogenous deliverance. Among these compounds, diazeniumdiolates, so-called NONOates, were developed. The release of NO occurs *via* a proton-catalyzed decomposition of these molecules, in neutral or acidic aqueous solutions. In theory, 2 moles of NO are released per mole of NONOate. However some studies have shown that the decomposition reaction depends on (*i*) the nature and the concentration of the NONOate and (*ii*) the pH. So, it is now believed that the stœchiometry is not analytically 2:1 (NO:NONOate). In addition, several parameters strongly influence the decomposition half-life ($t_{1/2}$) of the diazeniumdiolates. Consequently, the differences in reactivity of the various synthesized NONOates offer a wide range of NO delivery choices whatever a rapid release of NO or, conversely, a slow one over a long period is required.

Few studies have focused on the analysis of the kinetics of NO generation from diazeniumdiolates, although their knowledge is fundamental to foresee the amount of NO delivered when NONOates are used *in vivo* or *in vitro*. The lack of experimental data led us to investigate in details the decomposition kinetics of two commercially available and commonly used NONOates by performing the electrochemical determination of released NO with a home made NO-selective electrode. To do so, we selected the following NO donors: diethylammonium (*Z*)-1-(*N*,*N*-diethylamino)-diazen-1-ium-1,2--diolate (DEA-NONOate) and (*Z*)-1-[**N**-(2-aminoepropyl)-*N*--(2-ammoniopropyl)amino]-diazen-1-ium-1,2-diolate (PAPA-NONOate). This choice was driven by the fact that they have distinct half-life that cover a wide range of NO release rates (2 and 20 min at 37 °C, respectively). Control experiments were conducted on the electrochemical sensor to ensure the non-electroactivity of native NONOate compounds and their decomposition products (free amine nucleophile). Experimental curves corresponding to NO production in aerobic conditions were then fitted with a theoretical model to determine the kinetics parameters of NO release. The obtained kinetics parameters were then used to predict the profile of NO-release in aerobic buffered solutions[1].

REFERENCE

1. Griveau S., Dumézy C., Goldner P., Bedioui F.: Elechem. Commun. *9*, 2551 (2007).

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## PP059

# *IN VIVO* ELECTROCHEMICAL DETECTION OF NITROGLYCERIN-DERIVED NO IN TUMOR-BEARING MICE

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Interest in elucidating the mechanisms of action of various classes of anticancer agents and exploring the pathways of induced nitric oxide (NO) release provides an impetus to conceive better designed approach to locally detect NO in tumors, *in vivo*. We report here on the use of an electrochemical sensor that allows the *in vivo* detection of NO in tumor-bearing mice. First, we performed the electrochemical characterization of a stable electroactive probe, directly injected into the liquid micro-environment especially created around the electrode in the tumor[1]. Second, the ability of the inserted electrode system to detect the presence of NO itself in the tumoral tissue was achieved by using two NO donors: one diazeniumdiolate, namely (*Z*)-1-[*N*-(2-aminoepropyl)-*N*-(2--ammoniopropyl)amino]-diazen-1-ium-1,2-diolate (PAPA-NO) (ref.[1]), and nitroglycerin NTG. These NO donors allowed proving the electrochemical detection of intratumoral NO by (*i*) biomimetically induced endogenous release of NO in the tumoral tissue upon intratumoral injection of PAPA-NO or (*ii*) intra-peritoneal injection of NTG (Fig. 1). Indeed, it is know that NTG is metabolized in the vascular system and thus NTG-derived NO is produced and diffuses into the surrounding tissues.

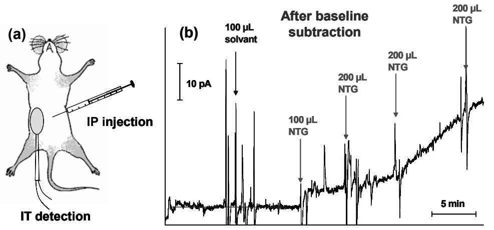

Fig. 1. **(a): schematic drawing of the tumor-bearing mouse showing the intra-peritoneal injection and the intratumoral detection sites; (b) intra tumoral chronoamperogram obtained at 0.85 V/ Ag-AgCl at the NO sensor upon injection of solvent and NTG** (1 mg mL$^{-1}$ in methanol)

This approach allows us to detect NO *in vivo* locally and in a real-time manner. It could be applied to the *in vivo* study of anticancer drug candidates acting on NO pathways.

REFERENCE

1. Griveau S., Dumézy C., Séguin J., Chabot G., Scherman D., Bedioui F.: Anal. Chem. *79*, 1030 (2007).

## PP060

# A CONSTRUCTION KIT FOR ELECTROANALYSIS INCLUDING THERMOELECTROCHEMICAL TECHNIQUES

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In older times, electrochemists were tinkers. They used to build, by their own hands, their first potentiostats. Later on, they became pioneers in computer control of measuring processes. Nowadays, nearly exclusively, commercial electrochemical instruments are in use. As a side effect of this development, it became unusual to enjoy experimenting with instrumental techniques and to design new electrochemical procedures.

In the presented project, a complete electrochemical instrument is designed with resources available to everybody. It consists of two major parts:

1. A simple analog unit (mainly a potentiostat) built with cheap operational amplifiers. It may, or may not, supplemented by modern electrode heating equipment[1].
2. A microcontroller circuit executing the measurement and sending the results to a pc.

The process is controlled by means of a “supervising program” written in a generally available programming language, namely Visual Basic for Applications (VBA). This is delivered with Microsoft Office. For the operator, the measurement is carried out by means of an “animated Excel sheet”. After pressing the “start” button in this sheet, the operator sees how rows of numbers are delivered and how the voltammogram (or any other electrochemical diagram) is building up before his face.

By means of the existing prototype, any commercially available electrochemical techniques like DPV, chronopotentio-metry, etc. can be applied. Furthermore, modern thermoelectro-chemical techniques like TPV (temperature pulse voltammetry) are included[2].

The system allows development of new methods by graphic design at the screen. The software can be extended in many directions, if wanted. The VBA program will be published as an “open source” project in internet.

REFERENCES

1. Wachholz F., Gimsa J., Duwensee H., Grabow H., Gründler P., Flechsig G.-U.: Electroanalysis *19*, 535 (2007).
2. Gründler P., Flechsig, G.-U.: Microchim. Acta *154*, 175 (2006).

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## PP061

# SCREEN-PRINTED ELECTRODES FOR HEAVY METALS MONITORING IN SEA WATER

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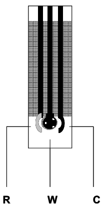
Nowadays there is an increasing demand on the determination of traces of heavy metals in the environment. The most used techniques for the analysis of trace amounts of metals are those based on optical methods. Beside some advantages they present several drawbacks when dealing with complex environmental matrices such as sea water. Electrochemical stripping analysis based on heavy metal accumulation and further stripping from the working electrode sensing surface represents another alternative. In our work, the measuring system is based on the use of screen printed electrodes (SPE) which allow an easy electrochemical stripping ensuring high sensitivity in detection.[1,2] These techniques are indicated for the direct monitoring of heavy metal traces in sea water allowing an *in-situ* control of pollution[3,4].



In this study, simultaneous detection of lead and cadmium contained in sea water in the low μg L$^{-1}$ (ppb) range have been carried out by using SPEs. Typical limits of detection using this type of SPEs are 2 and 3 ppb for Pb(II) and Cd(II) respectively. Moreover, the accuracy of the method was validated by comparison with the well-established anodic stripping voltammetry using the mercury electrode.

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REFERENCES

1. Palchetti I., Laschi S., Mascini M.: Anal. Chim. Acta *530*, 61 (2005).
2. Laschi S., Palchetti I., Mascini M.: Sens. Actuators, B *114*, 460 (2006).
3. Merkoçi A., Castañeda M. T., Alegret S.: *Stripping Analysis of Heavy Metals by Using Mercury Free Composite Based Sensors*. Chapter at 'Pure & Applied Analytical Chemistry', (Research SignPost, E. Palomar, ed.) p. 1–22, 2005.
4. Merkoçi A., Alegret S.: *Graphite-Epoxy Electrodes for Stripping Analysis*, Chapter 7 at Volume 49 “Electrochemical Sensor Analysis”, (Alegret, Merkoçi, ed.) Comprehensive Analytical Chemistry, p.143–161. Elsevier B.V., 2007.

### PP062

## SWNT-PRUSSIAN BLUE NANOCOMPOSITE MODIFIED SCREEN-PRINTED CARBON ELECTRODES USED FOR ALKYLPHENOLS DETECTION

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Alkyl phenols are of increasing concern due to their chemical functional similarity to estrogen and other hormones, binding to the estrogen receptor and inducing certain estrogen-specific biological responses *in vitro*[1–5]. For determination of nonyl-phenol and respectively octyl-phenol, screen-printed electrodes were modified with a new nanocomposite material obtained by combination of Prussian blue mediator with single-walled carbon nanotubes (SWNT/PB/3SPE). The biological element (horseradish peroxidase-HRP 5 mg $mL^{-1}$) was immobilized on the PB/SWNT modified screen-printed electrodes by different procedures (ex. entrapment in sol-gel matrices, adsorption and cross-linking with glutaraldehyde), allowing the determination of 4-*n*-nonylphenol and 4-*t*-octylphenol based on the electrochemical detection.

This PB/SWNT nanocomposite had synergistic effect on the catalysis towards $H_2O_2$ with highly satisfactory analytical behavior, with excellent sensitivity of 119.62 mA $M^{-1}$ $cm^{-2}$, a detection limit of 0.4 μM and fast response time of 13 seconds. The PB/SWNT modified screen-printed electrodes could amplify the reduction current of $H_2O_2$ by ~24 times, when compared with SWNT modified screen-printed electrodes.

Further, amperometric measurements were performed with biosensors obtained by immobilization of HRP entrapped in sol-gel matrix onto the SWNT/PB/3SPE electrodes. The experiments were carried out in phosphate buffer 0.05 M, pH 7.4, containing 60 μM $H_2O_2$ at an applied potential of −0.05 V *vs.* Ag/AgCl. The sensitivity of 4-*t*-octylphenol detection was 10.247 mA $M^{-1}$ $cm^{-2}$ with a detection limit of about 1.39 μM, while for detection of 4-*n*-nonylphenol the obtained sensitivity was about 9.872 mA $M^{-1}$ $cm^{-2}$ and the detection limit was 0.484 μM (S/N=3).

*We acknowledge financial support from MECT contract no. 5928/2006, 51-006/2007, 11-055/2007.*

REFERENCES

1. Tobata A., Kashiwada S., Ohnishi Y., Ishikawa H., Miyamoto N., Itoh M., Magara Y.: Water Sci. Technol. *43*, 109 (2001).
2. Magliulo L., Schreibman M. P., Cepriano J., Ling J.: Neurotoxicol. Teratology *24*, 71 (2002).
3. Rose A., Nistor C., Emneus J., Pfeiffer D., Wollenberger U.: Biosens. Bioelectron. *17*, 1033 (2002).
4. Jiang L. Y., Wang R. X., Li X. M., Jiang L. P., Lu G. H.: Electrochem. Commun. *7*, 597 (2005).
5. Tsai Y. C., Li S. C., Chen J. M.: Langmuir *21*, 3653 (2005).

### PP063

## RESOLUTION OF HEAVY METAL MIXTURES FROM HIGHLY OVERLAPPED ASV VOLTAMMOGRAMS EMPLOYING A WAVELET NEURAL NETWORK

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Recent activity coupling chemometric procedures to improve performance of electroanalytical methods is pushing for better detection limits and selectivity[1,2]. Several reports show convenient results for the determination of analytes of interest in diverse samples with electrochemical techniques employing artificial neural networks as the main processing tool[3].

The present work introduces the determination of three heavy metals in water (lead, copper and cadmium) in presence of thallium and indium as interfering species. Voltammetry stripping technique is used in open atmosphere, with no degassing pretreatment needed, and posterior signal processing employing a wavelet neural network.

A graphite-epoxy composite has been used as working electrode, without any surface regeneration after each analysis. The voltammetric technique starts with 120 sec. of preconcentration time, after which stripping scan takes place. The concentration range studied had been from 0.4 to 20 ppm for both analytes and interferents.

The information contained in the voltammetric signal is related with the concentration of each component under study, so that, it constitutes the input data for training and testing the WNN. A total of five networks were programmed with architecture of 153×4×5 and employing a k-fold cross validation method in each case.

When obtained *vs.* expected values were compared, correlation coefficients exhibited for the test subset where up to 0.996 for lead, 0.989 for cadmium and 0.995 for copper. Such a procedure may be representing a trend in electroanalysis consisting of mathematical treatment of overlapped signals in detriment of pre-treatment of the sample.

REFERENCES

1. Pravdova V., Pravda M., Guilbault G. G.: Anal. Lett. *35*, 2389 (2002).
2. Richards E., Bessant C., Saini S.: Electroanalysis *14*, 1533 (2002).
3. Moreno-Barón L., Cartas R., Merkoçi A., Alegret S., Gutierrez J. M., Leija L., Hernandez P. R., Muñoz R., del Valle M.: Anal. Lett. *38*, 2189 (2005).

## PP064
## VOLTAMMETRIC DETERMINATION OF DIAZINON IN COMERCIALLY AVAILABLE PRODUCTS

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Diazinon (*O*,*O*-diethyl *O*-2-isopropyl-6-methyl-pyrimidin-4-yl phosphorothioate) is an insecticide, which is often used in field crops and in household. It is important to develop methods for control of specific amounts of this compound due to its toxicity for living organisms. There are several analytical methods for establishing level of concentration for diazinon, namely: GC-MS, LC-MS, HPLC, biosensing or ELISA. Up to date only one electrochemical method was reported[1].

An adsorptive stripping voltammetric method for determination of diazinon based on its reduction reaction was developed. The electrode reaction was analyzed under conditions of square wave voltammetry (SWV). The peak current depends on the pH of the medium and instrumental parameters. Optimal conditions for quantitative determination were obtained in Britton-Robinson buffer at pH 4.5. Typical parameters were: frequency 100 Hz, amplitude 75 mV, step potential 5 mV, deposition time 60 s and deposition potential −0.4 V. Signal is a well defined cathodic peak at about −1.05 V *vs* Ag/AgCl. Linear range was from $2\times10^{-8}$ to $5\times10^{-7}$ mol $L^{-1}$. The voltammetric procedure was characterized with respect to the repeatability, precision and the recovery. The AdSWSV method was applied for determination of diazinon in several insecticide formulaes.

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REFERENCE

1. Carabias Martinez R., Becerro Dominguez F., Hernandez Mendez J., Gonzalez Martin P.: Electroanalysis *2* (7), 567 (1990).

## PP065
## ELECTROCHEMICAL METHODS – SENSITIVE TOOLS FOR DETECTION OF DNA DAMAGE

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DNA maintains, expresses and transfers to progeny genetic information in the cells. Damage to DNA arises from interactions of DNA with different chemical or physical agents occurring in the environment or in the cell. Unrepaired DNA damage may result in mutations and subsequently to development of severe diseases such as cancer.

DNA is an electro- and surface-active substance producing at mercury, carbon or some other electrodes analytically useful signals[1]. Some of them are sensitive to changes in the DNA structure. Behavior DNA at mercury or amalgam electrodes is strongly influenced by presence of DNA strand breaks. Biosensors for detection of DNA damage based on mercury or amalgam electrodes modified by supercoiled (sc) DNA and measurement of tensametric peak 3 were proposed[1]. Under certain conditions it is possible to detect a single lesion among $\sim10^5$ undamaged nucleotides with this type of DNA biosensor. This technique was adapted for detection of DNA base damage by application of DNA repair enzymes[2]. Damage to the DNA base is converted to a single strand break and changes in peak 3 heights are measured.

Recently we developed a new method for the detection of DNA damage based on combination of cleavage of damaged DNA by DNA repair enzymes and chemical modification of the enzymatically generated single-stranded regions by osmium tetroxide, 2,2'-bipyridine complex (Os,bipy)[3]. DNA-Os,bipy adducts are determined voltammetrically at pyrolytic graphite electrode. We show that this approach offers similarly efficient discrimination between intact and subtly damaged DNA as the technique based on utilization of tensametric peak 3 measured at mercury electrodes. Moreover, the Os,bipy marker-based technique works well in connection with linear chromosomal DNA. Its application is thus not limited to purified plasmid scDNA.

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REFERENCES

1. *Electrochemistry of nucleic acids and proteins Towards electrochemical sensors for genomics and proteomics*, (Palecek E., Scheller F., Wang J., ed.), Vol. 1, p. 74. Elsevier, Amsterdam 2005.
2. Cahova-Kucharikova K., Fojta M., Mozga T., Palecek E.: Anal. Chem. *77*, 2920 (2005).
3. Havran L., Vacek J., Cahová K., Fojta M.: Anal. Bioanal. Chem., in press.

## PP066
## ENVIRONMENTAL ASPECTS OF GSH REDOX REGULATION AND OXIDATIVE STRESS

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The redox regulating glutathione (GSH) system plays a vital role in living organisms in protecting cells against oxidative damage. There are indications that susceptibilities of different individuals to environmentally induced diseases (diabetes, brain damage and cancer) are associated with GSH

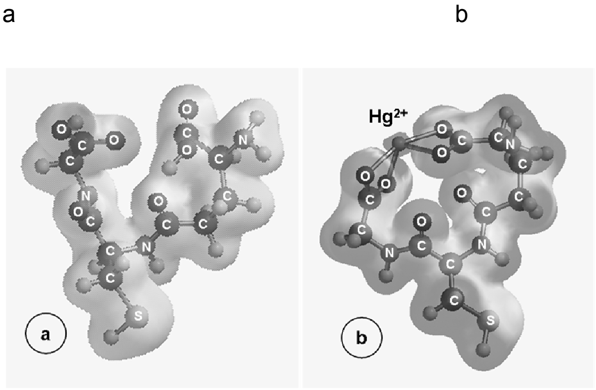

Fig. 1. **Electron density surfaces with mapped electrostatic potential for: (a) GSH and (b) $Hg^{2+}$-GSH mimicking $Ca^{2+}$-GSH chelate**

level in cells and body fluids. The interactions of GSH with various toxicants are suspected to influence the regulating capacity of GSH/GSSG system. We have investigated GSH interactions with toxic heavy metal ions[1,2] on electrodes using electrochemical quartz crystal nanogravimetry and immittance spectroscopy. We report here on Hg(II)-GSH interactions. We have found that the modification of a Au substrate with self-assembled glutathione (Au-SG) film creates a framework of confined-space microenvironment with ion-channels for enhanced $Hg^{2+}$-GSH interactions and rich charge transfer reactivity. The reduction of Hg(II) on a Au-SG piezoelectrode has been investigated in two regimes of ion channel permeation of the modifying film, at opened and closed ion channels. The maximum surface coverage determined from upd-Hg mass: $\theta_{Hg} = 0.31$. The chelation of $Hg^{2+}$ to carboxylate moieties at the outer film-solution boundary and place–exchange of Hg/ Au atoms at the sulphur root of adsorbed GSH have been further investigated[3] by *ab initio* quantum mechanical calculations.

The electronic structure of $Hg^{2+}$-GSH chelate was found to mimic that of $Ca^{2+}$-GSH chelate. The implications of this finding for studies of environmental effects on susceptibility to degenerative diseases should be of great significance.

REFERENCES

1. Hepel M., Tewksbury E.: J. Electroanal. Chem. *552*, 291 (2003).
2. Hepel M., Tewksbury E.: Electrochim. Acta *49*, 3827 (2004).
3. Hepel M., Dallas J.: in press.

## PP067
## ELECTROCHEMICAL STUDY OF INTERACTIONS OF NUCLEIC ACIDS WITH ELLIPTICINE USING MINIATURIZED ELECTRODES

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Ellipticine (5,11-demethyl-6*H*-pyridol(4,3-b)carbazole) is a plant alcaloid isolated from *Apocyanaceae* family (e.g. *Ochrosia borbonica*, *Excavativa cocinea*). This compound and some its derivatives exhibit significant antitumour activity. Mechanism of ellipticine antitumour consists in DNA intercalation and/or topoisomerase II inhibition. It was shown that ellipticine activated by cytochrome P450 is able to bind covalently to deoxyguanosine in DNA structure. The aim of this work was to study of interaction of ellipticine and DNA using miniaturized electrodes.

In our experiments the fabricated carbon paste printed electrodes modified with carbon nanotubes were used. The first step was to study of ellipticine‘s (0.5, 1 μM) electrochemical behavior by using cyclic and square wave voltammetry. In voltammograms obtained the oxidation signals in potential of about 600 mV were observable. Further the electrochemical properties of dsDNA were studied. The detection limit of dsDNA was below 1 $\mu g\ ml^{-1}$ and single bases were distinguished. In the following experiments the interaction of ellipticine and DNA was investigated. To the solution (50 mM potassium phosphate buffer, pH 7.4) different concentrations of ellipticine were added. To these reaction mixtures different amounts of dsDNA were added (to final concentrations from 0.5 to 10 $\mu g\ ml^{-1}$). From the obtained voltammograms the changes connected with ellipticine-DNA interactions were obvious. The oxidation signals of DNA decreased with increasing ellipticine concentration. The decrease of single bases oxidation signal can relate with structural changes in DNA caused by ellipticine intercalation. It clearly follows from the results obtained that our method using the manufactured miniaturized electrodes can be employed for DNA intercalation studies.

*We gratefully acknowledge the GA AV KAN208130801 for financial support to this work.*

REFERENCE

1. Dracinsky M., Sejbal J., Rygerova B., Stiborova M.: Tetrahedron Lett. 48, 6893 (2007).

## PP068

## INVESTIGATION OF INTERACTIONS OF MATRIX METALLOPROTEINASES WITH COLLAGEN BY CHRONOPOTENTIOMETRIC STRIPPING ANALYSIS

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Matrix metalloproteinases (MMPs) represent a family of structurally related zinc-dependent metallopeptidases. MMPs are able to degrade both majority and minority components of extracellular matrix include the native helix of collagen. These enzymes take part in normal biological processes such as ontogenesis or wound healing but also in inflammatory, generative, and especially malign processes. Zinc ion plays structural and regulatory role in MMPs but it is mainly involved directly in the catalytic hydrolysis of protein substrates.

The aim of this work was to propose and optimize the chronopotentiometric stripping analysis (CPSA) in connection with adsorptive transfer technique (AdTS) for MMP-9 detection. The method has been further employed to investigate MMP-9 interaction with collagen. Thanks to AdTS CPSA at hanging mercury drop electrode we were able to measure 5 μl sample volume. We optimized the following parameters: time of the accumulation of the sample on HMDE surface and the composition of supporting electrolyte. The suitable parameters were accumulation time of 90 s for both MMP-9 and collagen and supporting electrolyte Britton Robinson buffer (pH 5). The study of the MMP-collagen interaction was carried out as follows: *i*) collagen was accumulated on the surface of the working electrode and measured by the optimized method, *ii*) collagen was accumulated on the surface, then MMP-9 was accumulated on the modified surface of the working electrode and the measurement was carried out again under the same experimental conditions. The signal height after MMP accumulation increased for more than 100 % compared to collagen signals. It clearly follows from the results obtained that this technique can be considered as promising tool to investigate MMP-collagen interactions.

*We gratefully acknowledge the GA AV IAA401990701 for financial support to this work.*

REFERENCE

1. Kizek R., Vacek J., Trnkova L., Klejdus B., Havel L.: Chem. Listy *98*, 166 (2004).
2. Masarik M., Stobiecka A., Kizek R., Jelen F., Pechan Z., Hoyer W., Jovin T. M., Subramaniam V., Palecek E.: Electroanalysis *16*, 1172 (2004).

## PP069

## MULTICOMMUTATED ANODIC STRIPPING VOLTAMMETRY AT TUBULAR BISMUTH FILM ELECTRODE FOR LEAD DETERMINATION IN GUNSHOT RESIDUES

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When a firearm is discharged, a cloud of vapours and particulate material, called gunshot residues (GSR), is blasted more intensely onto the regions close to the gun. The determination of lead in GSR is a common practice in scientific criminal investigation. Over the years this metal has been qualified and quantified by many different analytical techniques including atomic absorption spectroscopy, scanning electronic microscopy and anodic stripping voltammetry at mercury film electrodes.

In this work an automated flow methodology based on a tubular electrochemical detector coupled to a multicommutated flow system was developed and applied to the determination of lead in GSR. The exploitation of the analytical potential of multicommutated flow systems allowed the implementation of an expeditious and easily controlled on-line standard addition method without sample handling and therefore with decreased risk of sample contamination.

The analytical cycle begins with the sequential aspiration of 10 μL of sample and carrier (Bi(III) 10.0 mg $L^{-1}$, acetate buffer 0.1 mol $L^{-1}$, pH 4.5) solutions during 2 minutes at a flow rate of 0.5 ml $min^{-1}$. The solution is propelled to the detector and the Bi(III) and Pb(II) are co-deposited at −1.5 V on the surface of a tubular carbon paste electrode. After deposition step, 2.0 mL of carrier solution are pumped through the electrochemical cell at a flow rate of 30.0 mL $min^{-1}$. An anodic scan from −1.0 to 0.0 V is afterwards applied in the stop flow modality. In the optimal experimental conditions, a linear calibration curve was obtained in the concentration range 0.1–10.0 mg $L^{-1}$ for a deposition time of 60 s, with a detection limit of 80.0 μg $L^{-1}$. The influence of potentially interfering ions on the stripping peak of lead was also evaluated. The procedure was applied to the analysis of 22 handgun GSR. Lead residues were found in the range from 5.0 to 80.0 μg $sample^{-1}$, the results are similar to those obtained in other ASV works for GSR. Validation of the results was performed by comparison with AAS.

*The authors thank the CONACyT (project 61310) and the Consejería de Educación y Cultura de la Junta de Castilla y León (project VA029A07) for financial support.*

## PP070
## INVESTIGATION OF AN AMPEROMETRIC FLOW INJECTION ANALYSIS BIOSENSOR BASED ON SULFIT OXIDASE FOR SULFITE MEASUREMENTS

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Sulphite is widely used as a preservative and antioxidant in food industry[1]. However, below authorized limit value, it can cause asthmatic attack and allergic reactions in sulphite-sensitive individuals[2]. To assure the quality control in food manufacturing, a sensitive, selective, rapid, simple and low cost method is required for sulphite determination.

Principle of the sulphite determination by biosensor presented here is based on the enzyme reaction of sulphite oxidase (SOD) prepared from chicken liver in our laboratory. The difficulty in the detection of enzyme activity is that the substrate (sulphite) and the product (hydrogen peroxide) show similar electrochemical activity. Therefore the parameters of measurement have to be adjusted to get amperometric signal only from one compound. Simple glassy carbon electrode pre-treatment processes that increase the sulphite or hydrogen peroxide signal separately are described.

In the FIA measurement blind or enzyme cell was used and amperometric cell is placed separately. The changes of signal generated by the enzyme can be followed with subtraction of the two (blind and enzyme) signals. The thin-layer enzyme cell developed by us[3], consisting of a protein membrane for immobilizing the enzyme, was fixed together with a Teflon plate supplied with a channel to ensure flow-through between two Plexiglass blocks (Fig. 1).

During the optimization of the biosensor the effects of temperature, flow rate, pH and ionic strength of the buffer, background electrolyte, and molybdenum concentration were investigated.

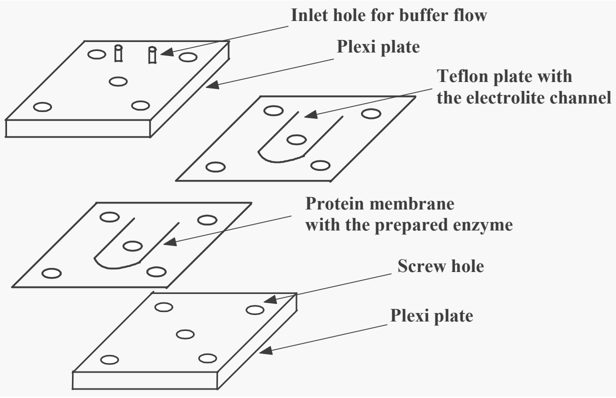

Fig. 1. **Structure of thin layer enzyme cell**

*This study was supported by EgerFood Regional Knowledge Center application 9/2005.*

REFERENCES

1. Zhao M., Hibbert D. B., Gooding J. J.: Anal. Chim. Acta *556*, 195 (2006).
2. Situmorang M., Hibbert D. B., Gooding J. J., Barnett D.: The Analyst *124*, 1775 (1999).
3. Adányi N., Tóth-Markus M., Szabó E. E., Váradi M., Sammartino M. P., Tomassetti M., Campanella L.: Anal. Chim. Acta *501*, 219 (2004).

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## PP071
## THE DETECTION OF Cd AND Pb IN SOIL SOLUTION BY DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

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Heavy metals in soil solutions are mostly bound in complexes with low molecular weight organic acids (LMWOA)[1]. The complexes occurrence is strongly depended on pH. Some of heavy metal complexes with LMWOA are also electrochemically detectable. The differential pulse anodic stripping voltammetry was used with HMDE for detection of Cd and Pb complexes with LMWOA.

In *in situ* sampled soil solutions[2] the Cd and Pb complexes were found from willow and alpine penny-cress planted in contaminated Fluvisol. In all soil solutions was found the peak in potential at about −540 mV. This peak potential was near the peak potential of $Cd^{2+}$ and probably belonged to Cd complex. The second peak, also in all focused solutions, occurred in −440 mV and belonged to Pb complex. The smaller signal of this peak was in the soil solution from alpine penny-cress. The existence of all founded metal complexes is confined to neutral or weakly acidic ambient. In acidic ambient (pH 2) in model and soil solution (after acidification) did not exist any Pb or Cd complex, all Cd and Pb were present in free ionic forms. The response in −530 mV by the acidification decreased comparing to −540 mV peak. It points to mixed Cd-Pb complex formation in pH 6. This idea is supported by the Pb behaviour. The Pb was distributed into two complexes, because after acidification to pH 2 was observed the peak belonging to Pb ion (−350 mV) higher than expected single Pb complex in −440 mV.

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REFERENCES

1. Wenzel W. W., Wieshammer G.: Int. J. Environ. Anal.

Chem. *59* (2–4), 277 (1995).
2. Jaklová Dytrtová J., Šestáková I., Jakl M., Száková J., Miholová D., Tlustoš P.: Cent. Eur. J. Chem. *6* (1), 71 (2008).

## PP072
## THE COMPLEXES OF Cd AND Pb WITH OXALIC ACID

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The potential risk of soil contamination with heavy metals and possibilities of phytoextraction in relation with solubilization of heavy metals using low molecular weight organic acids were discussed. However the problem with reliable *in situ* determination of defined heavy metals forms (in the meaning of a real molecule or ion) did not exist. The LMWOAs outside the plant[1] and phytochelatins inside the plant[2,3] play an important role in the puzzle of questions.

The Cd and Pb complexes with oxalic acid (OA) were detected in model solution using differential pulse anodic stripping voltammetry and differential pulse cathodic stripping voltammetry. Recording of the voltammograms was carried out by means of classical assembly of three electrodes, using HMDE as a working electrode, Ag/AgCl/KCl$_{sat.}$ as a reference electrode and Pt as an auxiliary electrode. The pH of the model solutions were adjusted to pH 7 with sodium hydroxide.

A mixed complex consisting of Cd, Pb and OA was found, its peak potential varies from −582 to −542.5 mV (*vs.* Ag/AgCl-/KCl$_{sat.}$) and depends on the Pb:Cd or Cd:Pb ratio. The "single" complexes of OA with Pb and Cd (Pb-OA and Cd-OA) are constrained on specific conditions. The existence of all focused metal complexes is confined to neutral or weakly acidic ambient. In acidic ambient (pH 2) in model and soil solution does not exist any Pb or Cd complexes, all Cd and Pb were presented in free ionic forms.

*This work was supported by the grant GAČR (Czech Science Foundation) No 521/06/0496.*

REFERENCES

1. Jones D. L., Dennis P. G., Owen A. G., van Hees P. A. W.: Plant Soil *248*, 31 (2003).
2. Šestáková I., Vodičková H., Mader P.: Electroanalysis *10*, 764 (1998).
3. Yosypchuk B., Šestáková I., Novotný L.: Talanta *59*, 1253 (2003).

## PP073
## APPLICATION OF MULTI-WAY CHEMOMETRICS TECHNIQUES FOR ANALYSIS OF AC-VOLTAMMETRIC DATA

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Copper damascene electrodeposition is a commonly used process for filling submicron trenches and vias for copper interconnect applications in advanced semiconductor devices. Organic additives, present in concentrations ranging from less than one to several hundred parts per million, control the structure and physical properties of the deposited metal[1–3]. Accurate concentration monitoring and control of these ingredients in electroplating baths are essential to satisfying the manufacturing process specifications for such devices.

Commonly used organic additives include: suppressors[1], usually high molecular weight polyglycols, that inhibit the rate of copper deposition at the tops of the trenches and vias, and accelerators[2,3], sulfur-containing compounds, that facilitate accelerated growth of the deposit at the bottom of the feature. As a result, defect-free bottom-up filling of the features (superconformal deposition) is achieved.

*In-situ* analysis of these organic additives is extremely challenging due to their competing functions, various chemical structures, wide range of concentrations, and the presence of accumulating degradation products[4,5].

The subject of this investigation was a commercial copper plating bath (Cu PC75, Technic, Inc.), which consisted of five components: copper (II) ion (from copper sulfate), sulfuric acid, chloride ion, suppressor, and accelerator with nominal concentrations of 0.275 M, 1.80 M, 1.5 mM, 5.00 ml l$^{-1}$, and 5.00 ml l$^{-1}$, respectively. The validity of this approach was verified on voltammetric data for the suppressor that was based on seven different voltammograms, having various waveforms, recorded for the training set solutions (Fig. 1).

Three multi-way calibration techniques were applied to

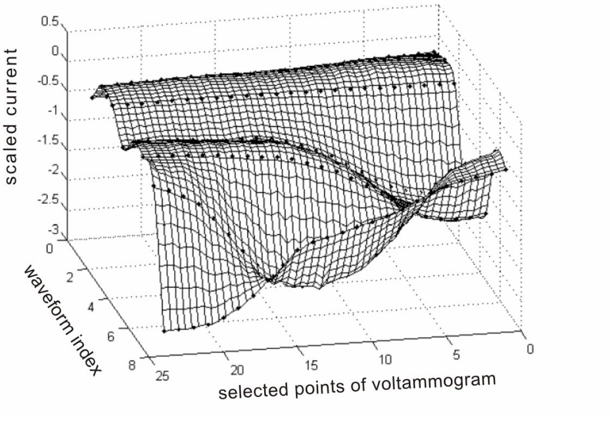

Fig. 1. **Three-way voltammetric data obtained for a solution of Cu PC75 containing 3 ml/l of suppressor**

determine the suppressor concentration in industrial copper electroplating baths used in semiconductor manufacturing. PARAllel FACtor analysis (PARAFAC) for multi-way array decomposition[6,7], coupled with Inverse Least Squares (ILS) regression (PARAFAC/ILS), Direct TriLinear Decomposition (DTLD) coupled with ILS (DTLD/ILS), and multi-linear Partial Least Squares (N-PLS)[7] regression were employed to develop and test calibration models based on trilinear AC-voltammetric data. All these techniques produced reliable calibration models, and provided quantitative information about the robustness of the models.

These models enable efficient utilization of highly informative AC-voltammograms resulting in calibration models with accurate predictive capabilities. An approach based on coupled SIMCA modeling power and LSR was used to determine optimum range(s) of various voltammograms (waveforms) analyzed as two-way data sets and subsequently taken to form a three-way data set employed for regression calculation. An application of Mahalanobis distance utilizing PARAFAC and DTLD scores was employed for outlier detection both within the training set and for the external validation data. This approach has a huge potential for statistical process control applications. The predictive performance of three methods: PARAFAC/ILS, DTLD/ILS and N-PLS were compared for suppressor calibration.

REFERENCES

1. Healy J., Pletcher D., Goodenough M.: J. Electroanal. Chem. *338*, 155 (1992).
2. Healy J., Pletcher D., Goodenough M.: J. Electroanal. Chem. *338*, 167 (1992).
3. Healy J., Pletcher D., Goodenough M.: J. Electroanal. Chem. *338*, 179 (1992).
4. Dietz K.: CircuiTree *13*, 22 (2000).
5. Dietz K.: CircuiTree *13*, 54 (2000).
6. Bro R.: Chemometrics Intell. Lab. Syst. *38*, 149 (1997).
7. Smilde A., Bro R., Geladi P.: *Multi-Way Analysis in Chemistry*. John Wiley & Sons, Chichester 2004.

## PP074

## USAGE OF CARBON PASTE ELECTRODE MODIFIED BY SWNT

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Carbon nanotubes (CNT), discovered in 1991 (ref.[1]), are a new type of carbon material with unique structural, geometric, mechanical and chemical properties. There are two types of CNT, single-wall (SWNT) and multi-wall carbon nanotubes (MWNT). SWNT, consisting of hollow cylindrically wound grapheme sheet, are real single large molecules. CNT can behave as metals or semiconductors depending on the structure and their unique properties make them very attractive for the design of electrochemical biosensors[2]. MWNT are more often used for the preparation of carbon paste electrode[3–6].

Carbon paste electrode modified by 10, 20 or 30 % (m/m) of SWNT was tested for determination of epinephrine and compared with bare carbon paste electrode. Carbon nanotubes were purified by a treatment with a concentrated nitric acid as written in literature[7]. The carbon paste was prepared by mixing the carbon powder with CNT and mineral oil. The paste was carefully hand-mixed for about half an hour in a mortar. The volume of 1 ml of the measured solution was used employing the carbon paste in miniaturized body of electrode. DPV measurements were performed in an unstirred and not de-aerated Britton-Robinson (B-R) buffer at a laboratory temperature. The influence of pH on voltammetric behaviour of epinephrine in B-R buffer pH 2–12 was studied and the results show, that the higher amount of SWNT contained the carbon paste the higher peak of epinephrine was obtained. B-R buffer pH 6 was chosen as optimal media for measurement with all types of carbon paste electrode.

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REFERENCES

1. Ijima S.: Nature *354*, 56 (1991).
2. Zhao Q., Gan Z., Zhuang O.: Electroanalysis *14*, 1609 (2002).
3. Rivas G. A., Rubianes M. D., Pedano M. L., Ferreyra N. F., Luque G. L., Rodriguez M. C., Miscoria S. A.: Electroanalysis *19*, 823 (2007).
4. Zheng L., Song J.: Talanta *73*, 943 (2007).
5. Chicharro M., Sanchez A., Bermejo E., Zapardiel A., Rubianes M. D., Rivas G. A.: Anal. Chim. Acta *543*, 84 (2005).
6. Rubianes M. D., Rivas G. A.: Electroanalysis *17*, 73 (2005).
7. Valentini F., Amine A., Orlanducci S., Terranova M. L., Palleschi G.: Anal. Chem. *75*, 5413 (2003).

## PP075

## THE USE OF NON-TRADITIONAL CARBON FILM ELECTRODE FOR VOLTAMMETRIC DETERMINATION OF 8-AMINOQUINOLINE

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Aminoquinolines belong to dangerous genotoxic substances[1] which can occur in environment[2]. They are closely related to amino derivatives of polycyclic aromatic hydrocarbons (APAH) known as carcinogenic and mutagenic compounds.

Therefore, 8-aminoquinoline (8-AQ), earlier determined using different types of working electrodes[3,4], have been chosen as a model substance for testing newly developed carbon film electrode[5]. Thanks to the presence of amino group on aromatic system, 8-AQ is easily electrochemically oxidizable compound. Therefore, there is a possibility to determine it on the basis of anodic oxidation using direct current voltammetry (DCV) and differential pulse voltammetry (DPV).

As a working electrode the carbon film modified silver solid amalgam electrode (CF-AgSAE) was used. It was constructed by covering the surface of silver solid amalgam electrode (AgSAE) by the carbon film. Carbon film was prepared by immersing AgSAE's surface to carbon ink prepared by mixing carbon powder and polystyrene in dichlorethane.

In the contribution, the optimal conditions (pH of base electrolyte) and parameters of DPV and DCV determination of 8-AQ using CF-AgSAE, as linear concentration range, limits of detection and repeatability of measurements, will be discussed.

Moreover, the application of these methods for determination of 8-AQ in model samples of drinking or river water with 8-AQ will be described.

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REFERENCES

1. http://monographs.iarc.fr/monoeval/crthgr02a.html, accessed 10. March 2005.
2. May W. E., Wise S. A.: Anal. Chem. *56*, 225 (1984).
3. Barek J., Fischer J., Navrátil T., Pecková K., Yosypchuk B., Zima J.: Electroanalysis *19*, 2003 (2007).
4. Stoica A. I., Zima J., Barek J.: Anal. Lett. *38*, 149 (2005).
5. Yosypchuk B., Barek J., Fojta M.: Electroanalysis *18*, 1126 (2006).

## PP076

## CATALYTIC ADSORPTIVE STRIPPING VOLTAMMETRIC DETERMINATION OF COBALT AND NICKEL AT THE SILVER AMALGAM FILM ELECTRODE

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The utility of the cylindrical silver-based amalgam film electrode (Hg(Ag)FE) of prolonged analytical application in catalytic adsorptive stripping voltammetry (CAdSV) was examined. The advantages of this sensor, very convenient and providing good analytical performance in anodic voltammetry[1,2] and chronopotentiometry[3], have already been described.

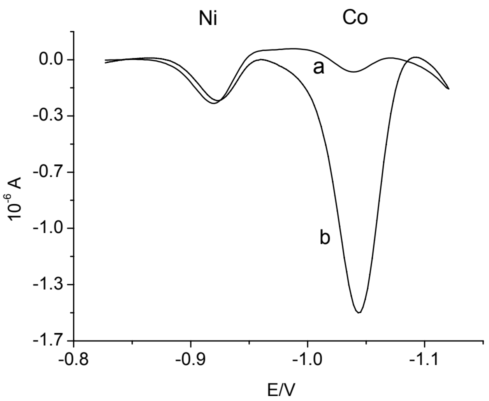

Fig. 1. **DP-CAdSV voltammograms of $1\times10^{-9}$ M Co and $1\times10^{-8}$ M Ni in a supporting electrolyte containing 0.1 M ammonia buffer (pH 9.2) and $5\times10^{-5}$ M nioxime before** (curve a), **and after addition** (curve b) **of 0.4 M nitrite ions**. $E_{dep}$ −0.7 V, $t_{dep}$= 60 s

In this work, the Hg(Ag)FE electrode has been applied for the simultaneous determination of cobalt and nickel by means of adsorptive stripping voltammetry.

The method is based on adsorptive accumulation of analytes at the Hg(Ag)FE, in a supporting electrolyte consisting of 0.1 M ammonia buffer and $5\times10^{-5}$ M cycloheksanedione dioxime, and on the utilization of the catalytic enhancement of the cobalt response in the presence of nitrite ions (Fig. 1).

The optimal composition of the supporting electrolyte and the instrumental parameters (i.e. pulse amplitude, accumulation potential and accumulation time) of the determination of Co and Ni traces were selected. The detection limit obtained for a 60 s accumulation time was estimated to be $5.8\times10^{-11}$ M (0.0035 μg L$^{-1}$) for Co and $2.2\times10^{-10}$ M (0.013 μg L$^{-1}$) for Ni. The repeatability of peak current was 5.8 % and 5.6 % for Co and Ni, respectively. The calibration plots were linear from 0.01 to 7 μg L$^{-1}$ for Co and from 0.1 to 10 μg L$^{-1}$ for Ni. Finally, the Hg(Ag)FE was applied to determine nickel and cobalt in certified reference material, with satisfactory results.

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REFERENCES

1. Baś B., Kowalski Z.: Electroanalysis *14*, 1067 (2002).
2. Baś B.: Anal. Chim. Acta *570*, 195 (2006).
3. Kapturski P., Bobrowski A.: Electroanalysis *19*, 1863 (2007).

## PP077

## ADVANCED APPROACH FOR LACTATE OXIDASE IMMOBILIZATION ONTO SILOXANES MEMBRANES FOR CONSTRUCTION OF PRUSSIAN BLUE BASED BIOSENSORS

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For a long time we have been developed the approach for oxidases immobilization using the advanced immobilization protocol based on a non-aqueous immobilization route with high content of organic solvent[1]. Combination of effective hydrogen peroxide transducer based on electrodes modified with Prussian Blue and novel method for enzyme-containing membranes formation from the media with high content of organic solvent, allow to develop the effective amperometric first generation biosensors with low detection limits[2].

In current study we have used siloxanes of different structures $PhSi(OMe)_3$, $MeSi(OEt)_3$, $ViSi(OEt)_3$, $\gamma$-$NH_2PrSi(OEt)_3$ for immobilization of lactate oxidase (LOD) from *Pediococcus species* on screen-printed electrodes modified with Prussian Blue (PB). The immobilization of LOD in siloxanes was carried out from water-organic mixtures with high content of organic solvent. Lactate biosensors were prepared by casting the LOD/siloxane mem-branes over PB modified planar electrodes. The developing low cost and mass-productive Prussian Blue based LOD biosensors have advanced analytical characteristics: improved sensitivity and signal-to-noise ratio, low detection limit, high operational stability to compare with known analogs.

Planar biosensors were used for express detection of lactate in flow-injection and periodic regimes. Lactate biosensors were applied for the analysis of lactic acid in fermented beverages (bread kvass).

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REFERENCES

1. Karyakin A. A., Karyakina E. E., Gorton L., Bobrova O. A., Lukachova L. V., Gladilin A. K., Levashov A. V.: Anal. Chem. *1996,* 4335.
2. Karyakin A. A., In: *Encyclopedia of Sensors*. Vol. 1, p. 329. Am. Sci. Publ. 2006.

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## PP078

## ELECTROCHEMILUMINESCENCE OF $Ru(bpy)_3^{2+}$ INCORPORATED IN LANGMUIR-BLODGETT FILMS OF NAFION

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The use of Nafion modified electrodes is based on the ion-exchange selectivity, pre-concentration capabilities as well as mechanical robustness and chemical and biological inertness of the ionomer. Notwithstanding the easiness of preparation and good performance of cast-coated or spin coated Nafion electrode, significant improvements can come from the development of deposition procedures able to achieve a better control of the deposition at a molecular level. Operating in this direction, recently, we developed original methods for preparing ultrathin films of Nafion and other ionomers by using the Langmuir-Blodgett (LB) technique.

Such modified electrodes have been characterized electrochemically and by epifluorescence microscopy[1], using $Ru(bpy)_3^{2+}$ incorporated in the Nafion LB films as luminescent probe. The results of these measurements showed the compactness of the film and the homogeneity of the distribution of the analyte incorporated in the film. On the other hand, small apparent diffusion coefficient[1] characterize the Nafion LB films, which are for $Ru(bpy)_3^{2+}$ in the range $1\times10^{-12}$ – $8\times10^{-12}$ $cm^2 s^{-1}$.

In the present work, we apply a different luminescent technique that is electrochemically induced luminescence or electrochemiluminescence (ECL), for the same redox probe incorporated in the LB Nafion coating, deposited onto transparent ITO (indium-tin oxide) electrodes.

In this case, luminescence is produced by chemical reaction between electrogenerated $Ru(bpy)_3^{3+}$ and a suitable co-reactant that can be cationic tripropylamine (protonated) or anionic oxalate[2]. The luminescence generated at the modified electrode is recorded by a photomultiplier connected with an oscilloscope, while applying an oxidation potential (from 0.8 V to 1.2 V) with the co-reactant either dissolved in solution or loaded (when possible) in the LB film.

In particular we focused on the role of the LB film on the luminescence, studying carefully the role of the luminescence generating reaction when it takes place inside the ionomeric coating or at the polymer/solution interface. The results obtained indicate that ECL at the Nafion LB films: (*1*) is characterized by a faster response time than ECL at cast-coated electrodes; (*2*) gives a linear calibration plot only at low concentrations of co-reactant; (*3*) increases linearly with the number of Nafion LB layers increase; (*4*) is characterized by different intensities when $Ru(bpy)_3^{2+}$ is present both in solution and in the film or only inside the Nafion film.

These characteristics are discussed in terms of reaction mechanism and structure of the Nafion LB film.

REFERENCES
1. Moretto L. M., Kohls T., Chovin A., Sojic N., Ugo P.: Langmuir, *in press*.
2. Pastore P., Badocco D., Zanon F.: Electrochim. Acta *51*, 5394 (2006).

## PP079

## THIN-FILM APPROACHES FOR THE FABRICATION OF DISPOSABLE BISMUTH-FILM ELECTRODES FOR TRACE METAL ANALYSIS BY STRIPPING VOLTAMMETRY

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Although mercury has been the commonest electrode material in stripping analysis for detection in the cathodic potential region, both metallic mercury and the mercury salts used to generate mercury–film electrodes (MFEs) are toxic and are considered undesirable. A few years ago, a new type of electrochemical sensor, the bismuth-electrode (BiFE) -consisting of a thin "film" of metallic bismuth on a conductive substrate-, has been proposed as an electrode that could potentially substitute the poisonous mercury electrodes commonly employed in stripping analysis[1]. Research over the last five years, has shown that the performance of the BiFE in stripping analysis is analogous to its mercury counterparts, mercury-film electrodes (MFEs)[2,3]. Several methods for the generation of the bismuth film have been reported but the most widely used method for the preparation of BiFEs is electroplating which is usually carried out potentiostatically from a Bi(III) dolution (either *in situ* or *ex situ*) [2,3]. However, electroplating involves the use of Bi(III) salts, complicates the experimental procedure and requires a conductive substrate.

In this work, a novel method for preparation of bismuth sensors is proposed, based on sputtering of a silicon wafer with a thin film of bismuth[4]. This alternative approach for the generation of the bismuth film has some distinct advantages compared to electroplating: *i*) the use of Bi(III) ions is avoided and, therefore, the experimental procedure is simplified; *ii*) a conductive substrate is not necessary, because the sputtered bismuth coating serves as both the sensing element and the current transducer; *iii*) the fabrication parameters (such as electrode geometry and bismuth film thickness) can be easily controlled while a highly reproducible surface coverage is obtained, and; *iv*) the use of standard thin-film technology offers increased scope of mass-production of inexpensive and disposable devices.

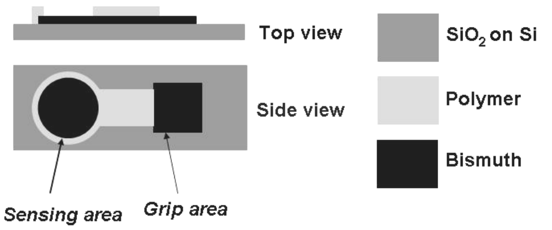

Fig. 1. **A lithographically-fabricated disposable bismuth-sputtered electrode**

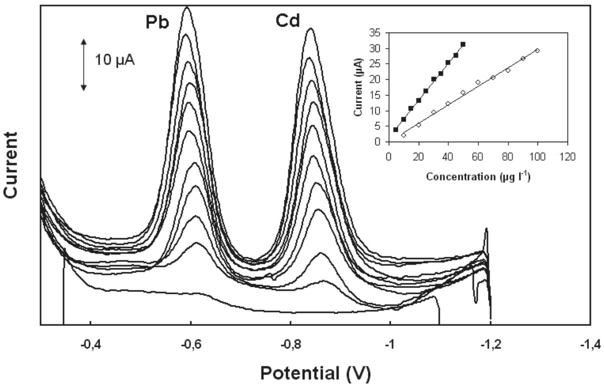

Fig. 2. **Stripping voltammograms for the simultaneous determination of Pb(II)** (steps of 5 μg L$^{-1}$) **and Cd(II)** (steps of 10 μg L$^{-1}$) **by SWASV on a lithographically-fabricated disposable bismuth-sputtered electrode** (inset is the calibration graph: ■ Pb; ○ Cd)

Different configurations of bismuth-sputtered sensors are created and presented using both lithographic and non-lithographic approaches. A typical bimuth-covered electrode fabricated by lithography is illustrated in Figure 1.

Results obtained for the analysis of Cd(II) and Pb(II) using square-wave anodic stripping voltammetry (SWASV) and of Ni (II) and Co(II) using square-wave adsorptive stripping voltammetry (SWAdSV) demonstrate "proof-of-principle" of these devices and suggest that these mercury-free electrodes are suitable as disposable sensors for trace metal analysis. Typical stripping voltammograms for the simultaneous determination of Cd(II) and Pb(II) are illustrated in Figure 2.

REFERENCES
1. Wang J., Lu J. M., Hocevar S. B., Farias P. M. A., Ogorevc B.: Anal. Chem. *72*, 3218 (2000).
2. Economou A.: Trends Anal. Chem. *24*, 334 (2005).
3. Wang J.: Electroanalysis *17*, 1341 (2005).
4. Kokkinos C., Economou A., Raptis I., Efstathiou C. E., Speliotis T.: Electrochem. Commun. *9*, 2795 (2007).

## PP080
## NOVEL APPROACHES TO ELECTROCHEMICAL DETECTION OF POLYMORPHISMS IN DNA SEQUENCES

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The current rapid progress in biomedicine and biotechnology is connected with increasing requirements for new rapid and cheap methods allowing detection of subtle changes in DNA sequences. Among other techniques, a great attention is paid to electrochemical methods.

DNA is an electroactive molecule yielding various types of signals on mercury, carbon and other types of solid electrodes[1]. Despite the fact that some of them are sensitive to small changes in DNA sequence and DNA damages, for various reasons techniques utilizing electrochemical DNA tags and indicators (intercalators, groove binders or covalently bound tags) are recently preferred. Among others, we use osmium tetroxide complexes with nitrogen ligands, mainly Os,bipy (bipy - 2,2'-bipyridine)[2]. Os,bipy reacts selectively with ssDNA, exhibiting a strong preference to thymine residues; the adducts are electrochemically active and very stable.

We designed single-stranded (ss) and double-stranded (ds) oligonucleotides (ODNs) containing various number of single-base mismatches or abasic sites, treated them with Os,bipy and measured signal of the DNA-Os,bipy adduct. For the analysis we utilized recently developed so called "double surface" technique involving separation on magnetic particles[2,3]. In model experiments we first labelled ss ODNs with various number of thymine residues (differing in only one base) by the Os,bipy complex. As we expected the signal of osmium increased with increased number of thymine residues. The same principle we used for detection of single base mismatches (G•T, T•T), insertions or abasic sites in intra- and intermolecular DNA duplexes. We show that Os,bipy was able to react with unpaired or mispaired T. Number of the mismatches can be estimated in this way. This approach appears promising as a new technique for electrochemical SNP detection.

*This work was supported by GACR (203/08/P598, 203/07/1195), Ministry of Education, Youth and Sports of the CR (LC06035) and by a Institutional Research Plans No.AVOZ50040507 and AV0Z50040702.*

REFERENCES

1. *Electrochemistry of Nucleic Acids and Proteins Towards Electrochemical Sensors for Genomics and Proteomics* (Palecek E., Scheller F., Wang J., ed.), Vol. 1, p. 74–174. Elsevier, Amsterdam 2005.
2. Fojta M., Kostecka P., Trefulka M., Havran L., Palecek E.: Anal. Chem. *79*, 1022 (2007).
3. Fojta M., Havran L., Billova S., Kostecka P., Masarik M., Kizek R.: Electroanalysis *15*, 431 (2003).

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## PP081
## THE INVESTIGATIONS OF POLYMERISATION AND DEGRADATION PROCESSES OF POLYANILINE BY MEANS OF ELECTROCHEMICAL QUARTZ CRYSTAL NANOBALANCE (EQCN)

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Electrochemical Quartz Crystal Nanobalance (EQCN) enables to detect very small changes of mass of about $10^{-9}$. Such a sensitive method in connection with electrochemical methods makes it possible to follow very small changes of the mass of a working electrode. The application of this method to examine conductive polymers enables the quantitive determination of changes proceeding during the growth of a polymer layer also during the work of a polymer-covered electrode. It offers the possibility to examine not only the electropolymerisation processes but also the properties of polymer layers[1,2].

The objects of our experiments were Polyaniline and its co-polymers with anthranilic and metanilic acids. All examined layers were obtained by means of electrochemical polymerization. The measurements were carried out in aqueous solutions of supporting electrolytes containing perchloric acid or sulphuric acid. The aim of the research was to determine the quantitive changes during the polymerisation, the changes caused by the processes of reduction and oxidation of the polymer layer, and the changes connected with the degradation of the polymer layer.

When it was possible, we compared the changes of the amount of the polymer calculated on the basis of the measurement of the charges with the results obtained by EQCN, receiving consistent results. We obtained the dependences connecting the changes of the polymer mass with the potential

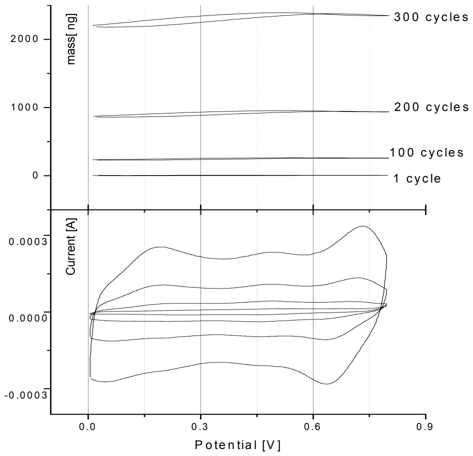

Fig. 1. **Voltammetric and electrogravimetric curves of polymerisation of aniline + anthranilic acid** in solutions 0.5 M $HClO_4$ and 0.5 M $NaClO_4$; 2, 100, 200 and 300 cycles, $v = 200$ mV $s^{-1}$

and time of degradation. The apparatus used in the experiment consisted of the electrochemical quartz crystal nanobalance M 106 (Uelko) and the potentiostat PAR 273 working under the control of the software CorrWare v.2.9 (Scribner Associates Inc.).

REFERENCES

1. Hepel M.: *Interfacial Electrochemistry, Theory, Experiment, and Applications*, p. 599–630. M. Dekker, New York 1999.
2. Szumacher R.: Angew. Chem. Int. Ed. Engl. *29*, 329 (1999).

## PP082
## A PULSE VOLTAMMETRIC ELECTRONIC TONGUE TO PREDICT BISULFITES IN WINES

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According with the remarkable development in the design of electronic tongue devises at present, these apparatus represent a good alternative to be used in the characterization of the chemical composition of wines. In the specific case of electronic tongue based on voltammetry, several works have been presented applied in the food industry, and more specifically, in the wine industry. Voltammetry represents an extensively used technique in analytical determinations due to, in first place, its high sensitivity. When you faced measurements in a complex media, in which many redox active species were present (i.e. wines) pulse voltammetry appears to be a suitable method to be used.

In this paper, a method for predicting bisulfites in wine by using an electronic tongue based on pulse voltammetry is proposed. Previous studies have shown the capabilities of this electronic tongue to monitor quality changes of milk[1], recognize different microbial species[2], and for supervision of rinses in a washing machine[3].

*Apparatus*

*ET*. The electronic tongue devise consists in a four working electrodes array (gold, rhodium, iridium and stainless steel, all with purity of 99.9 % and 1 mm diameter) housed inside a stainless steel cylinder used at the same time as both the body of the ET system and the counter/reference electrode, and with a self polishing devise incorporated as well.

*Samples*

Although the main objective of this study is the prediction of bisulfites in wine, others compounds have been included on this analysis in order to create an experimental design with a system of 3 compounds-3 levels. Ascorbic acid and Histamine are also included in the analysis. The compounds are different in structure and redox activity, although they are frequently present in wines composition (bisulfites and ascorbic acid as additives and histamine as a spoilage indicator). By using a software of experimental design (MODE 8.0), the quantity of samples is generated, as well as the levels of the compounds on each sample is established to compile all information of the 3x3 system for further statistical analysis. Thus, a calibration set including 18 samples was prepared by addition of the three selected compounds into a wine matrix (white wine Bereich Nierstein purchased from the local market Systembolaget); in levels low (0), medium (2) and high (4). The numbers to define levels do not correspond with concentrations. For prediction, another set including 20 samples prepared in different wine matrixes was prepared as well. Prediction set includes also levels 1 and 3.

The measured data was analyzed by multivariate analysis, including Principal Component Analysis (PCA), Cross-validation and Partial Least Squared (PLS), the latest for building prediction models. Figures 1 and 2 show the Predicted *vs.* Measured data of bisulfite for calibration set and both calibration/prediction sets together respectively. The

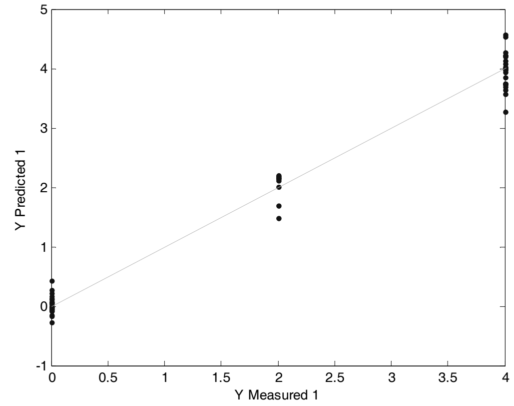

Fig. 1. **PLS model for calibration set (bisulfite)**

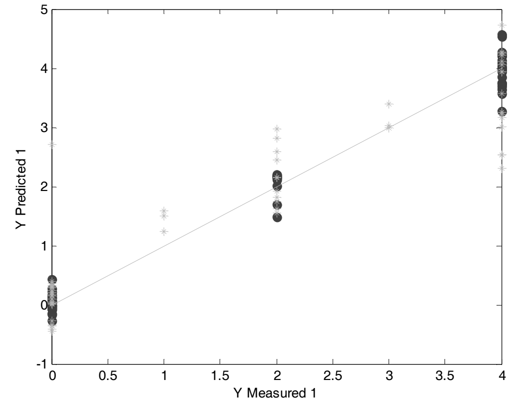

Fig. 2. **PLS model for calibration (•)/prediction (*) set (bisulfite)**

accuracy of prediction for bisulfites resulted to be higher than both ascorbic acid and histamine, owing mainly the higher redox activity of bisulfites in front of the used electrodes.

REFERENCES

1. Winquist F., Bjorklund R., Krantz-Rulker C., Lundstrom I., Ostergren K., Skoglund T.: Sens. Actuators, B *111*, 299 (2005).
2. Soderstrom C., Winquist F., Krantz-Rulker C.: Sens. Actuators, B *89*, 248 (2003).
3. Ivarsson P., Johansson M., Hojer N., Krantz-Rulker C., Winquist F., Lundstrom I.: Sens. Actuators, B *108*, 851 (2005).

## PP083

## HIGHLY SENSITIVE DETERMINATION OF THIOL COMPOUNDS BY LIQUID CHROMATOGRAPHY WITH AMPEROMETRIC DETECTION AT A SILVER-BASED CARBON PASTE ELECTRODE

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Endogenous thiol derivatives such as cysteine and glutathione are nowadays well recognized as biomarkers in oxidative stress conditions. Homocysteine has been shown to be a marker of the risk of adverse cardiovascular events. Drug compounds such as captopril and *N*-acetylcysteine are widely applied as pharmaceuticals. Numerous analytical methods have been described for the assay of thiol compounds but there is still a need for method improvement in terms of sensitivity and selectivity.

We are in the process of developing an amperometric detector for the highly sensitive quantification of thiol compounds. A thin-layer flow through amperometric detector cell featuring a solid carbon paste working electrode containing 35 % of micronized metallic silver was applied in the present study. The working electrode has so far been shown to be sensitive to cysteine, *N*-acetylcysteine, homocysteine, reduced glutathione (GSH) and halogenides i.e. species known to strongly interact with Ag and $Ag^+$.

Mechanistic informations regarding the sensing process have been obtained by hydrodynamic and cyclic voltammetry.

An anion exchange liquid chromatography (formic acid buffer pH 3.5 containing 10 mM of sodium nitrate and 10 % acetonitrile as mobile phase) was applied to separate the studied thiols from the halogenides. The working potential was fixed at 0.080 V *vs.* Ag/AgCl. A linear relationship between peak current and GSH concentration was obtained from 10 nM to 100 nM. Beyond 100 nM, the repeatabilty of successive injections resulted in a progressive decrease in the signal (anodic current) but application of a suitable negative potential for 5 min permitted to reestablish the detector's sensitivity.

## PP084

## DIFFERENTIAL PULSE CATHODIC STRIPPING VOLTAMMETRIC ANALYSIS FOR INORGANIC As (III) AND TOTAL INORGANIC ARSENIC IN GRAPE JUICES

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Bentonite, volcanic clay, is a technological aid widely used in grape juice to remove proteins, thus reducing the risk of protein haze. However, the bentonite can have arsenic as a contaminant transferring it to the beverage.

This study describes a fast, simple and inexpensive differential pulse cathodic stripping voltammetric method performed on a hanging mercury drop electrode (HMDE) for determination As (III) and total inorganic arsenic concentrations at $\mu g\ L^{-1}$ level in samples of grape juices available in the Brazil.

Electroactive As (III) is determined by direct CSV analysis and total arsenic is determined after reduction of As (V) to As (III). As (V) is calculated by difference between total inorganic arsenic and As (III). Sodium metabisulfite and sodium thiosulfate were used for the reduction of As (V) to As (III). As (III) is then determined in 0.4 mol $L^{-1}$ HCl, 5 mg $L^{-1}$ Cu (II) and 0.004 mg $L^{-1}$ Se (IV) supporting electrolyte.

At optimized conditions, the detection limits for both As (III) and As (V) were 0.2 $\mu g\ L^{-1}$ for a deposition time of 180 s the linear range being from 0.5 to 50 $\mu g\ L^{-1}$.

Standard deviation for 1 $\mu g\ L^{-1}$ arsenic concentration (n=10) was 5 %. The method has been successfully applied to identify and quantify inorganic arsenic in grape juices and the accuracy was verified by a recovery test on spiked samples (98.2 %).

Interference from some ions in grape (Pb, Cu, Zn, Cd) is minimal.

Twelve different brands of grape juice were analyzed and the concentration range for As (III) was 51–71 $\mu g\ L^{-1}$ and As (V) 34–60 $\mu g\ L^{-1}$.

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REFERENCES

1. Catarino S., Madeira M., Monteiro F., Rocha F., Curvelo-Garcia A. S., Sousa B.: J. Agric. Food Chem. *56*, 158 (2008).
2. Ferreira M. A., Barros A. A.: Anal. Chim. Acta *459*, 151 (2002).
3. Herce-Pagliai C., Moreno I., Gonzalez G., Repetto M., Cameán A. M.: Food Addit. Contaminants *19*, 542 (2002).

## PP085

## TOWARDS Q-PCR OF *Escherichia coli* WITH IMPROVED ELECTROCHEMICAL DETECTION

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Outbreaks of foodborne disease caused by *E. coli* bacteria have become a serious problem. While there are many types of *E. coli* bacteria, only certain types are caused of important foodborne illness, as the harmful foodborne strain called O157:H7. These pathogenic strains of *E. coli* are found in undercooked meat, lettuce, unpasteurized milk, apple juice and contaminated well water[1]. In food and environmental samples responsible for disease, the levels of contamination are sometimes very low. Thus, very sensitive detection methods are required.

A very sensitive assay for the electrochemical detection of *Escherichia coli* based on DNA biosensors has been designed. The electrochemical detection is performed by the specific amplification of the *eaeA* gene, related with the pathogenic activity of these bacteria. The amplification is performed by Polymerase Chain Reaction (PCR) using labelled primers with biotin and digoxigenin, obtaining a double labelled amplicon with biotin and digoxigenin in each extreme, respectively. The amplified biological material is detected by two strategies based on *i*) bulk-modified composite with avidin as affinity biomolecule, obtaining high selective electrodes[2]; and *ii*) magneto sensors[3]. In the first approach, the double-labelled amplicon *i*) is directly linked to the avidin-modified biocomposite while in the second approach *ii*) it is previously immobilized on magnetic beads modified with streptavidin, followed by the magnetic capture of the beads by the magneto sensor. The electrochemical detection is finally achieved by an enzyme marker, based on HRP.

The combination of the genome amplification by PCR, capture of the double-tagged amplicon and electrochemical detection using a sensitive m-GEC electrode, provide promising results compared with Q-PCR based on TaqMan probes.

REFERENCES

1. Batt C. A., in: *Encyclopedia of Food Microbiol*. 633, Elsevier 2004.
2. Zacco E., Pividori M. I., Alegret S.: Biosens. Bioelectron. *21*, 1291 (2006).
3. Erdem A., Pividori M. I., Lermo A., Bonanni A., del Valle M., Alegret S.: Sens. Actuators, B *114*, 591 (2006).

## PP086

## ELECTROCHEMICAL MAGNETO IMMUNOSENSING AND GENOSENSING FOR FOOD SAFETY

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In recent years, a number of food-safety emergencies have shaken consumer confidence in the production of food and have focused attention on the way food is produced, processed, and marketed. Most of the agents found in food are natural contaminants from environmental sources, but some are deliberate additives. Although microbiological issues are the greatest concern[1], many consumers are worried about the long-term impact of mixtures of chemicals additives (such as pesticides and veterinary drug residues)[2]. As food regulatory agencies have established strict control programs in order to avoid food contaminants from entering the food supply, official laboratories should be able to efficiently process a high number of samples. As a result, routine, rapid and efficient food control becomes mandatory. Biosensors offer an exciting alternative to the more traditional methods for food analyses, allowing rapid ‘real-time’ and multiple analyses that are essential for the detection of contaminants in food[3].

One of the most promising materials is biologically modified magnetic beads based on the concept of magnetic bioseparation. Magnetic beads have brought novel capabilities to electrochemical immunosensing and genosensing. The development of magneto immunosensing and genosensing strategies with electrochemical detection is presented in this work. The strategy can be used to detect by immunological recognition pattern, pesticides, antibiotic residues, or can also be used to detect pathogenic bacteria or viruses such as *Salmonella*, *E.coli* or *Hepatitis*. The biological reaction for these assays was performed on magnetic beads and the electrochemical detection was based on HRP enzyme. In all cases, the modified magnetic beads were then attached to a novel magneto sensor based on graphite-epoxy composite for the electrochemical detection. These new assays offer great promises for rapid, cost-effective and on-site analysis of biological, food and environmental samples.

REFERENCES

1. Pividori M. I, Alegret S.: Comp. Anal. Methods *49*, 437 (2007).
2. Rooney R., Wall P. G., in: *Encyclopedia of Food Science and Nutrition,* p. 2682. Academic Press, 2003.
3. Mello L. D, Kubota L. T: Food Chem. *77*, 237 (2002).

## PP087

## DISPOSABLE MAGNETIC DNA SENSORS FOR THE DETERMINATION OF A SPECIFIC *Enterobacteriaceae* FAMILY GENE

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DNA sensors combined with magnetic separation constitute a time saving approach which may replace current lengthy enrichment protocols, also allowing the application of diverse end-point detection methods.

In this study, an enzyme-amplified strategy based on the coupling of streptavidin-peroxidase to biotinylated *lac z* gene target sequences has been developed. Previously, the biotinylated 25 mer capture probe was attached to streptavidin-modified magnetic beads, which were then immobilised at the surface of TTF modified screen printed gold electrodes (Au/SPE).

Amplification of the electrochemical signal was achieved coupling a ultrasensitive streptavidin-peroxidase polymer to the biotinylated target, after the hybridisation step and using TTF as redox mediator. The amperometric response obtained at –0.15 V after the addition of hydrogen peroxide was used to detect the hybridization process. In order to improve the sensitivity of the determination and reduce the assay time, different variables of the assay protocol were optimized. The stability and analytical characteristics of the sensor were evaluated and compared with those obtained in a previous work[1]. A low detection limit (5.7 fmol) with good stability ($RSD_{n=10}$ = 7.1 %) was obtained. The obtained results show the ability of the sensor for the detection of low amounts of target oligonucleotide, which is an advantage in the determination of microorganisms without the need of PCR amplification. The developed magnetic DNA sensor was used for the detection of *E. coli* in cell cultures with good results.

*The financial support of Santander/Complutense Investigation Project PR 27/05-13953 is gratefully acknowledged. Oscar A. Loaiza acknowledges a pre-PhD fellowship of the Universidad Complutense de Madrid.*

REFERENCE

1. Loaiza O. A., Campuzano S., Pedrero M., Pingarrón J. M.: Talanta *73*, 838 (2007).

## PP088

## NEW STRATEGY FOR SNPs DETECTION USING AN ELECTROCHEMICAL GENOSENSOR ARRAY

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This communication describes development and characterization of an electrochemical genosensing platform where genotyping of clinically relevant samples relied on an unusual hybridization strategy: the stacking hybridization.

Taking advantage from the peculiar interactions existing between two coaxially hybridized oligonucleotides, which respectively served as stabilizing oligo and allele-specific oligonucleotide (ASO) probe, this method allowed the unambiguous resolution of mismatched from matched duplexes (*yes* or *not* response).

All hybridization experiments were performed at capture probe-modified screen-printed gold arrays[1,2]. Accordingly, electrochemical transduction of the hybridization events was accomplished using a specific enzyme label, which converted its electro-inactive substrate into an electroactive derivative.

While optimizing the hybridization methodology, the performance characteristics of different pairs of coaxially hybridized probes were compared. The influence of parameters such as ASO probe length, relative position of the mismatched site and strength of the stacking interactions thus emerged.

Further characterization of the stacking hybridization process through melting experiments allowed a deeper understanding of how the mutual interactions between the oligos involved in the biorecognition process influenced selectivity and sensitivity of the assay.

To prove usefulness and general validity of the genotyping methodology, application of the analytical pathway was then demonstrated for human *TP53* gene.

Owing to its inherent selectivity, sensitivity and low cost, the proposed genotyping platform, implemented into an 8 electrodes array, thus represent a promising tool for the systematic screening of genes with mutational hotspots.

REFERENCES

1. Lucarelli F., Marrazza G., Mascini M.: Anal. Chim. Acta *603*, 82 (2007).
2. Farabullini F., Lucarelli F., Palchetti I., Marrazza G., Mascini M.: Biosens. Bioelectron. *22*, 1544 (2007).

## PP089

## TESTING OF BIODEGRADABILITY OF NON-IONIC SURFACTANTS USING THE INDIRECT TENSAMMETRIC TECHNIQUE COMBINED WITH A PTFE CAPILLARY TRAP

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The widespread use of detergents means that complete biodegradation of their main components – surfactants – is necessary. Different tests are used for investigating biodegradability. In screening tests, an investigated surfactant is the sole source of organic carbon, and a very simple biodegradation progress control such as $CO_2$ production, total organic carbon concentration or biological oxygen demand is sufficient. However in more complex cases, such as the continuous flow activated sludge test, a specific determination of the tested surfactant is necessary. This is very difficult in the case of non-ionic surfactants (NS), especially those without chromophoric groups such as oxyethylated alcohols. Use of the indirect tensammetric technique (ITT) combined with the PTFE capillary trap (PTFECT) significantly reduces such difficulties.

For NS determination, a small sample of a test effluent is pneumatically forced through a PTFECT, and the entrapped NS are eluted with ethyl acetate and determined using ITT with ethyl acetate as a monitor.

In order to demonstrate the potential of the proposed method, the biodegradability of oxyethylated alcohol C12E10 was tested under the conditions of the OCDE 301 test with activated sludge as inoculum. The concentration of C12E10 was determined daily. On the day of maximum biodegradation rate, the bacteria strain *Pseudomonas fluoresecens* was isolated from the tested mixture. These bacteria were augmented, and the test of C12E10 biodegradation was repeated with the augmented *Pseudomonas fluoresecens* as the inoculum. Immediate biodegradation of C12E10 was observed.

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## PP090

## INVESTIGATION OF THE MOBILITY OF THALLIUM IN THE ENVIRONMENT USING FLOW-INJECTION DIFFERENTIAL – PULSE ANODIC STRIPPING VOLTAMMETRY

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Thallium is an element which is highly toxic to humans, animals, micro-organisms and plants. The toxic effect of the element is closely related to its mobility. The main sources of thallium pollution are pyrites and lead-zinc ores. It is therefore the areas where these ores are mined and processed which are at the greatest risk of thallium pollution. For this reason the mobility of the element in soil and bottom sediment fractions and in surface water in those areas needs to be investigated. Flow-injection differential-pulse anodic stripping voltammetry (FI-DP-ASV) is an excellent tool for such investigation. FI-DP-ASV enables the thallium determination at concentrations of picomole per litre and medium exchange when the analysed soil or sediment fraction contains interferents.

The object of this work was to determine the mobility of thallium in soil and bottom sediments, as well as surface water, in an area of lead-zinc ore mining and processing near Olkusz (Poland). Several rivulets flowing in this area were investigated in terms of thallium concentration in fractions of bottom sediments, flood-plain terraces and in surface water. Sequential extraction of soil was performed in accordance with the BCR procedure. The link between ore processing and thallium concentration is clearly observable. However, the major part of thallium is contained in the primary parent matter and is basically immovable.

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## PP091

## NEW MONITORING SUBSTANCES FOR THE INDIRECT TENSAMMETRIC TECHNIQUE

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The indirect tensammetric technique (ITT) is limited in application to the determination of non-ionic surfactants (NS). This technique has been developed in order to overcome problems with the very complex tensammetric behaviour of surfactant mixtures. The lowering of the monitoring substance peak due to competitive adsorption of the investigated surfactants is the analytical signal in ITT. Usually a saturated solution of ethyl acetate is used as the monitor. Despite the limited range of application, ITT is very useful because of the widespread use of NS, their common presence in the aquatic environment, and the lack of better methods. So far saturated ethyl acetate has proved to be the best monitor. It forms a single well-shaped tensammetric peak which reacts approximately additively for different NS. No problems with surfactant mixtures are observed. Ethyl acetate reacts only to NS, while anionic surfactants are highly tolerated. However, the disadvantage of this monitor is the technically difficult stage of dissolution of ethyl acetate. This is the crucial obstacle to the automation of the whole measurement cycle.

The aim of this work was to identify another monitoring substance having the same advantages as ethyl acetate, but with better solubility in the supporting electrolyte. The expected properties are the formation of a single well-shaped tensammetric peak located at approximately −1.25 V *vs* SCE, and satisfactory solubility in the supporting electrolyte. Among the substances subjected to preliminary testing, two display these properties: pentanol and iso-hexanol (4-methyl-2-pentanol). The solubility of both substances in a supporting electrolyte is much higher than for ethyl acetate, and their peaks are located within the expected range. Both tested monitors responded to different concentrations of a model NS (Triton X-100). Γ-shaped calibration curves were recorded. Tolerance to an anionic surfactant – dodecylbenzene sulphonate – was checked.

## PP092

## SIMULTANEOUSLY VOLTAMMETRIC DETERMINATION OF DOPAMINE AND ASCORBIC ACID AT PLATINUM ELECTRODE MODIFIED WITH PEDOT-PRUSSIAN BLUE HYBRID FILMS

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The analytical determination of dopamine (DA) has attracted a great deal of interest due to its physiological role as neurotransmitter[1]. The electroanalysis of DA is hindered by the presence of other biologically active compounds, such as ascorbic acid (AA)[2]. Therefore, selectivity and sensitivity are important in the development of new electrochemical sensors for DA quantification. The use of electrodes modified with inorganic redox mediator and/or conducting polymers is very promising[3]. In this work, the voltammetric determination of DA in presence of AA at platinum electrodes modified with poly-[3,4-ethylenedioxythiophene] (PEDOT) and Prussian Blue (PB) hybrid films is reported. The hybrid inorganic-organic coating has been prepared by a two steps method. Firstly, the PEDOT film was deposited onto electrode surface by potentiodynamic polymerisation in aqueous solution in the presence of ferricyanide ions. The obtained ferricyanide-doped polymer film was transferred in iron (III) ions containing aqueous solution, where the electrode potential was cycled from 0.6 to −0.4 V *vs*. SCE. During the potential cycling PB is formed inside the PEDOT matrix. The composite modified electrode was investigated in buffered aqueous solutions by using cyclic voltammetry and square wave voltammetry. The electrocatalytic activity of the composite coating towards the dopamine oxidation has been also investigated. The composite coating showed a high electrocatalytic effect towards the dopamine oxidation in the presence of ascorbic acid. A linear dependence of the anodic peak currents from square wave voltammetry over the dopamine concentration ranging from $5\times10^{-5}$ to $6\times10^{-4}$ M, in the presence of $1\times10^{-2}$ M AA, was obtained. A detection limit (S/N = 3) of $2\times10^{-5}$ M has been also obtained. The new modified electrode could be used as electrochemical sensor for simultaneous determination of dopamine in the presence of a high amount of ascorbic acid.

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REFERENCES

1. Wightman M., May L. J., Michael A. C.: Anal. Chem. *60*, 769A (1988).
2. Selvaraju T., Ramaraj R.: Electrochem. Commun. *2*, 667 (2003).
3. Chen S.-M., Chzo W.-Y.: J. Electroanal. Chem. *587*, 226 (2006).

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## PP093

## ELECTROCHEMICAL DETECTION OF DOPAMINE AT PLATINUM ELECTRODE MODIFIED WITH INORGANIC-ORGANIC HYBRID MATERIALS

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The development of voltammetric sensors for the determination of dopamine has received a considerable interest during last few years. Dopamine (DA) is one of the important neurotransmitters widely distributed in the mammalian brain tissues[1]. A major drawback in the quantification of DA is the presence of interfering compounds such as ascorbic acid (AA). Both these compounds show closely voltammetric peaks at unmodified electrodes. Therefore, the use of electrodes modified with different mediators can solve this problem[2].

In the present contribution, the voltammetric determination of DA at platinum electrodes modified with hybrid inorganic-organic coating consisting of poly-[3,4-ethylenedioxythiophene] (PEDOT) and Prussian Blue (PB) is reported. The modified electrode was prepared by electrochemical polymerization of EDOT in aqueous solution containing potassium ferricyanide. The obtained polymer modified electrode was immersed in aqueous solution containing iron (III) chloride and the electrode potential was scanned from 0.6 to (−0.2) V *vs*. SCE. During the potential cycling the PB is formed inside the PEDOT matrix. The hybrid inorganic-organic coating exhibits good electrocatalytic properties in dopamine oxidation. In square wave voltammetry a linear response was obtained in the range of $1\times10^{-5}$ to $1\times10^{-3}$ M.

*The financial support from the Romanian Ministry of Education and Research through grant 2CEEX06 – 1143/25.07.2006 is gratefully acknowledged.*

REFERENCES

1. Selvaraju T., Ramaraj R: Electrochem. Commun. *5*, 667 (2003).
2. Jiang X., Lin X.: Anal. Chim. Acta *537*, 145 (2005).

## PP094

## VALIDATION OF ELECTROANALYTICAL METHOD FOR DOPAMINE DETERMINATION IN THE PRESENCE OF INTERFERENTS

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Many analytical methodologies, such as electrochemical, chromatographic, were established for the determination of dopamine (DA) in real samples[1–3]. In this paper a voltammetric method for the determination of DA in presence of ascorbic acid (AA) at platinum electrodes modified with poly-[3,4--ethylenedioxythiophene] (PEDOT) and Prussian Blue (PB) hybrid films is reported. The hybrid films have been prepared by potentiodynamic polymerisation of EDOT in aqueous solution in the presence of ferricyanide ions, followed by potential cycling in iron (III) ions containing aqueous solution. By this procedure a hybrid PEDOT-PB coating is obtained. The hybrid coating exhibited good electrocatalytic effects towards DA and AA oxidation. A decrease of anodic peak potentials of about 200 mV in comparison with the unmodified electrode was obtained. The response of the electrochemical sensor towards DA was linear over the concentration range from $5\times10^{-5}$ to $6\times10^{-4}$ M, in the presence of $1\times10^{-2}$ M AA. The detection limit (S/N=3) of $2\times10^{-5}$ M has been obtained. The results obtained through this electroanalytical method were validated and compared to analytical data obtained by high liquid performance chromatography.

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REFERENCES
1. Othman A. M., Rizka N. M. H., El-Shahawi M. S.: Anal. Sci. *20*, 651 (2004).
2. Studer L., Psylla M., Bohler B., Evtouchenko L.,Vouga C. M., Leenders K. L., Seller R. W., Spenger C.: Brain Res. *41*, 143 (1996).
3. Wang Y., Fice D., Yeung P.: J. Pharm. Biomed. Anal. *21* 519 (1999).

## PP095

## STUDY OF BASE SEQUENCES IN OLIGODEOXYNUCLEOTIDE NONAMERS BY ELECTROCHEMICAL AND CHROMATOGRAPHIC TECHNIQUES

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The structure of oligonucleotides (ODN´s) corresponds to their properties and behavior in organisms. This work deals with the study of electrochemical and chromatographic behavior of ODN´s in relation to sequences of nucleic acid bases in the ODN chain. Twenty ODN nonamers with different sequences of adenine (A) and cytosine (C) but with the same ratio of A:C (3:6) were investigated by high performance liquid chromatography (HPLC) with UV/Vis detection and by linear sweep voltammetry (LSV) and/or elimination voltammetry with linear scan (EVLS)[1–3]. In electrochemical methods our interest was focused on the reduction signals of A and C measured at mercury electrode, in separation method on retention times of ODN. Both electrochemical and chromatographic data obtained were consequently evaluated by artificial neural network (ANN). We constructed ANN models using different inputs including selected points of LSV or EVLS curves (peak heights of separated reduction signals of A and C or differences of reduction A and C potentials from EVLS curves) and retention times from HPLC measurements. Moreover we used supplementary parameters such as extinction coefficients at 260 nm, melting points, ΔH and ΔS of the stacking effect[5–6]. The best results were obtained from the model with the following inputs: 50 points from LSV curve taken at reference scan rate 200 mV $s^{-1}$, retention times and all supplementary parameters.

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REFERENCES
1. Trnková L., Jelen F., Postbieglová I.: Electroanalysis *15*, 1529 (2003).
2. Trnková L., Jelen F., Petrlová J., Adam V., Potěšil D., Kizek R.: Sensors *5*, 448 (2005).
3. Trnková L., Jelen F., Postbieglová I.: Electroanalysis *18*, 662 (2006).
4. Mikelová R., Trnková L., Jelen F., Adam V., Kizek R.: Electroanalysis *19*, 348 (2007).
5. http://biophysics.idtdna.com/
6. http://www.promega.com/biomath/calc11.htm

## PP096

## AMPEROMETRIC BIOSENSOR FOR DOPAMINE DETERMINATION BASED ON ELECTRODEPOSITION OF OVEROXIDIZED POLYPYRROLE ON SOL-GEL-DERIVED BIOSENSOR

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Conducting polymers such as polypyrrole, are being compared with the classical electrode materials such as metals and glassy carbon in electroanalytical applications and chemical sensors or biosensors[1]. Polypyrrole undergoes overoxidation at more alkaline media, has been regarded which leads to the loss of conductivity and dedoping. Several reports on the use of sol-gel chemistry in the development of biosensors have received extensively in the past few years[2–4]. Plant tissue containing the enzymes and these plants based biosensors offer a good alternative compared with biosensors based on isolated enzymes[5]. An amperometric biosensor based on overoxidized polypyrrole (OPPy) coated on sol-gel bioelectrode was developed by entrapment of plant tissue into sol-gel matrix. Polymer film was electrochemically synthesized by electrooxidation of 0.1 M pyrrole in aqueous solution onto the sol-gel biosensor. Amperometric measurements were performed at a constant potential of 0.4 V *vs.* SCE. The OPPy-modified sol-gel bioelectrode showed a high activity for the electrooxidation of dopamine (DA) at $E_p = 0.163$ V *vs.* SCE. The effects of pH, pyrrole concentration and potential range of polypyrrole overoxidation on the response of the electrode were elucidated. The modified bioelectrode presented a linear response range for DA from $9.99\times10^{-6}$ M upto $1.1\times10^{-3}$ M by amperometry. The diffusion coefficient of $6.86\times10^{-8}$ for DA was also obtained using chronoamperometry study. The response of the overoxidized polypyrrole coated sol-gel electrode and uncoated sol-gel electrode were compared. The sensitivity and the stability of the biosensor were also determined. The biosensor was applied for the determination of dopamine in pharmaceutical formulations.

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REFERENCES

1. Li Y. F.: Electrochim. Acta *42*, 203 (1997).
2. Majidi M. R., Jouyban A., Asadpour-Zeynali K.: J. Electroanal. Chem. *589*, 32 (2006).
3. Wang J., Pamidi P. V. A., Park D. S.: Electroanalysis *9*, 52 (1997).
4. Chen X., Dong Sh.: Biosens. Bioelectron. *18*, 999 (2003).
5. Felix F. S., Yamashita M., Angnes L.: Biosens. Bioelectron. *21*, 2283 (2006).

## PP097

## MULTISENSOR ANALYSIS OF HOMOLOGOUS NON-IONIC SURFACTANTS

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Quantitative non-ionic surfactant determination is a complex analytical problem as various composite mixes, wastewaters, sewage sludges, etc. contain mixtures of their isomers, homologues and oligomers. For detection polyoxyethylated alkylphenols and their degradation products in various objects different separation techniques with subsequent detection are used. To this end, spectrophotometry, solid-phase extraction with high-performance liquid chromatography and fluorescence, thin layer, gas chromatogramphys, chromato-mass-spectrometry are most often employed. Lately, multi-sensor systems with multivariate calibration technique ("electronic tongue") have been employed for fast qualitative and quantitative analysis of multi-component solutions. The basic requirements to an array sensor are a low selectivity and a high cross-sensitivity.

Samples of polyoxyethylated nonylphenols

$C_9H_{19}C_6H_4O(C_2H_4O)_mH$ (m = 10–100) with a purity of 96–98 % were investigated. Compounds of polyoxyethylated nonylphenols with barium and tetraphenylborate ions (for example, nonylphenol-12-Ba-tetraphenylborate) were used as electrode-active compounds of membranes sensitive to non-ionic surfactants.

Low selectivity, high cross-sensitivity of surfactant sensor, and also identity of their electrochemical and transport parameters are a basis for designing multi-sensor systems for determination of homologous non-ionic surfactants in various objects (model mixtures, artificial polluted natural waters).

Analytical signals from non-ionic surfactant sensor arrays were processed by partial least-squares algorithm (PLS) and artificial neural networks (ANN) with back propagation of errors. At PLS processing the responses from surfactant sensor arrays were randomly parted into a set for training (to create a model) and a reference one for checking its forecasting capacity. To employ the artificial neural network technique the data were randomly splitted into calibration, monitoring and validation sets. Three-layered neural networks were used. The number of neurons in the input layer corresponded to the number of sensors in the array. The concentration of non-ionic surfactants, for example, in the three-component model mixture ranged from $1\times10^{-5}$ to $2{,}2\times10^{-3}$ mol $l^{-1}$ for nonylphenol-10, $1\times10^{-5}$ – $2\times10^{-3}$ mol $l^{-1}$ for nonylphenol-30, $1\times10^{-5}$ – $3\times10^{-3}$ mol $l^{-1}$ for nonylphenol-40 at different component ratios. The mean relative error of homologous non-ionic surfactant detection was 7 to 9 % for PLS and 3 to 4 % for ANN. The results of neural network training can be used for analysis both three-component model mixtures and two- component model mixtures.

The possibility of designing of surfactant sensor arrays for separate definition of homologous polyoxyethylated nonylphenols in two-, three-, four-component systems (model mixtures and artificial polluted natural waters) is shown. The least relative errors of detection were obtained for ANN.

REFERENCES

1. Cantero M., Rubio S., Pérez-Bendito D.: J. Chromatogr., A *1067*, 161 (2005).
2. Castillo M., Martínez E., Ginebreda A., Tirapu L., Barceló D.: Analyst *125*, 1733 (2000).
3. Gundersen J. L.: J. Chromatogr., A *914*, 161 (2001).

## PP098

## HIGHLY SENSITIVE DETERMINATION OF IODIDE BY ION CHROMATOGRAPHY WITH AMPEROMETRIC DETECTION AT A SILVER BASED CARBON PASTE ELECTRODE

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A silver based carbon paste electrode was developed for use as detector in ion chromatography (IC) for the sensitive determination of iodide in real samples. Micro and nanoparticles of silver were investigated for different electrodes fabrication.

The iodide assay was based on ion chromatography with amperometric detection (IC-AD) at a silver composite electrode polarized at +0.080 V *versus* Ag/AgCl. Free iodide and organoiodide compounds were studied. The detection process was characterized by studying the redox behavior of iodide ions at both silver and silver composite electrodes by cyclic voltammetry. The presence of iodide ions in solution was found to considerably facilitate metallic silver oxidation, with response currents directly related to iodide concentration. The calibration curve at the selected silver composite electrode was linear in the concentration range comprised netween 0.635–63.5 $\mu g\ l^{-1}$ iodide. The relative standard deviation (RSD) for successive injections was below 3 % for all iodide standard solutions investigated. The limit of detection (LOD) was 0.47 $\mu g\ L^{-1}$ (3.7 $nmol\ L^{-1}$) for an injection volume of 20 μL, i.e. 74 fmol injected. The IC-AD method was successfully applied to the determination of iodide in complex real samples such as table salts, sea products and iodide bound drug compounds. The analytical accuracy was verified by the assay of iodide in milk powder from a iodide Certified Reference Material (CRM) BCR 150.

## PP099

## USE OF BISMUTH FILM ELECTRODE FOR THE CATHODIC ELECTROCHEMICAL DETERMINATION OF TRIAZINE HERBICIDES

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Since its introduction in stripping analysis[1], the bismuth film electrode (BiFE) has been accepted in many electroanalytical laboratories worldwide. BiFEs have found a wide range of application in anodic stripping voltammetry, potentiometric stripping analysis as well as in cathodic adsorptive stripping voltammetry for the determination of some metals. On the other hand, its application for the determination of organic compounds has been much less studied[2].

In this communication, a square wave cathodic voltammetry (SWCV) procedure for herbicides determination at an *ex situ* plated BiFE is described. Different herbicides with reductive moieties, emphasizyng in the triazine derivatives, were subjected to study. Carbon-based substrates have been studied for the preparation of *ex situ* bismuth film electrodes as well as the influence of relevant parameters upon the bismuth film formation (plating solution, deposition potential and deposition time).

The use of bismuth film electrode present advantages over the plain substrate electrodes such as low reduction overpotential and good stability for the electroanalysis of herbicides in acidic media even in the presence of oxygen and could be a good alternative to the toxic mercury-based electrodes.

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REFERENCES

1. Wang J., Lu J., Hocevar S. B., Farias P. A. M., Ogorevc B.: Anal. Chem. *72*, 3218 (2000).
2. Sánchez Arribas A., Bermejo E., Chicharro M., Zapardiel A.: Electroanalysis *18*, 2331 (2006).

## PP100

## SENSOR BASED ON ELECTROSPUN NYLON NANOFIBERS

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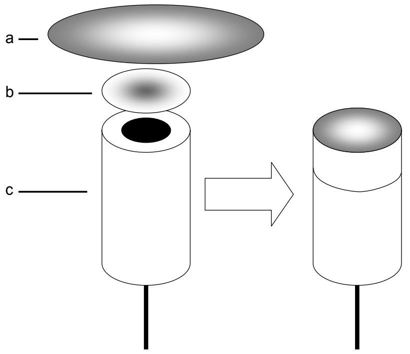
A web-like membrane consisting of nylon nanofibers, prepared by electrospinning, was used to produce an electrochemical biosensor for the sensible sensing of glucose[1]. Glucose oxidase was immobilized (*1*) by physical adsorption on the platinum electrode surface, (*2*) by physical adsorption through the nylon net, and (*3*) by chemical bonding between the enzyme and the membrane, with glutaraldheide as a cross-linker. In all the three set-ups, the advantages arisen by use of the nylon net were evident. The nylon nanofiber net exhibits an high surface to volume ratio compared with the usual thick nylon support. This allows unique chemical features that can be summarized as: (*a*) excellent support properties which prevent leakage of the enzyme; (*b*) selective physisorption of



Scheme 1. **Example a possible electrode assembly a) electrospun nanofiber b) layer of glucose oxidase immobilized by drop coating c) working electrode**

interpherents (such as polyphenols) by changing the protonation of nylon amine group, (*c*) prevention of the electrode passivation, (*d*) enhanced biosensors' longevity. The advantages of the new nanofibers strip-coated biosensor will be discussed via the electrochemical sensing of glucose in real food matrices.

*We thank Cariplo's Foundation.*

REFERENCE

1. Granato F., Scampicchio M., Bianco A., Mannino S., Bertarelli C., Zerbi G.: Electroanalysis, in press.

## PP101

## MICROCONTROLLER-BASED POTENTIOSTAT DEVELOPED USING THE LTCC TECHNOLOGY

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The miniaturization of amperometric chemical analyzers involves the dimensional reduction of electrodes to the micrometer scale. To generate stable potentials and to obtain precise measurements, high-sensitivity electronic circuits are required. The low temperature cofired ceramics (LTCC) technology has been widely applied to the production of multilayer printed circuit boards due to its excellent electrical, mechanical and thermal properties[1,2]. Its compatibility with serigraphic techniques and its fabrication process enable the aggregation of several layers to obtain multilayer circuits, which results in high-density boards of elevated complexity and small size. In this work, the development of a microcontroller-based potentiostat using LTCC technology is presented (see figure 1). Since the potentiostat is based on a microcontroller, several amperometric techniques can be applied (cyclic voltammetry, differential pulse voltammetry, square-wave voltammetry, etc.). The instrument was designed to work in four current ranges to improve sensitivity at different intensity levels. Results showed a high signal to noise ratio with a base line of ±0.5 nA, comparable with commercial instruments.

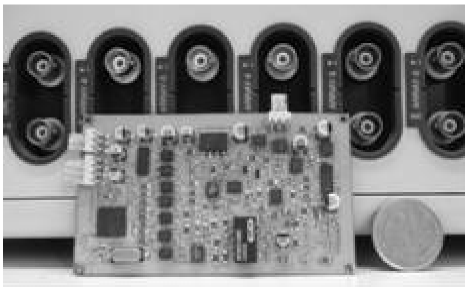

Fig. 1. **Microcontroller-based LTCC potentiostat**

Since the LTCC technology permits the fabrication of complex three-dimensional structures, microfluidic systems can be easily developed and integrated with electronics to obtain real micro total analysis systems (μTAS).

REFERENCES

1. Derenovsek A., Naeini G., Preu W., Wersing M., Eberstein W., Schiller J.: Eur. Ceram. Soc. *21*, 1693 (2001).
2. Wang G., Zhang G., Ma J.: Mater. Sci. Eng., B *94*, 48 (2002).

## PP102

## GENOSENSOR FOR SARS VIRUS DETECTION BASED ON GOLD NANOSTRUCTURED SCREEN-PRINTED CARBON ELECTRODES

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The present work describes the design of a genosensor for a sequence of the SARS virus using gold nanostructured screen-printed carbon electrodes (SPCEs) as transducers.

SPCEs are *in-situ* modified with gold in order to get nanostructured surfaces by applying a constant current intensity of −5 μA for 2 minutes using a 0.1 mM $AuCl_4^-$ acidic solution. The nanostructured obtained following this methodology is showed in Fig. 1.

The design of the genosensor consists on the immobilization of thiolated probe strands over the surface, and after a blocking step, hybridization with biotin labeled target strands is carried out. Then, streptavidin labeled with alkaline phosphatase is used to catalyze an enzymatic reaction that leads to the analytical signal; an electrochemical process of silver[1].

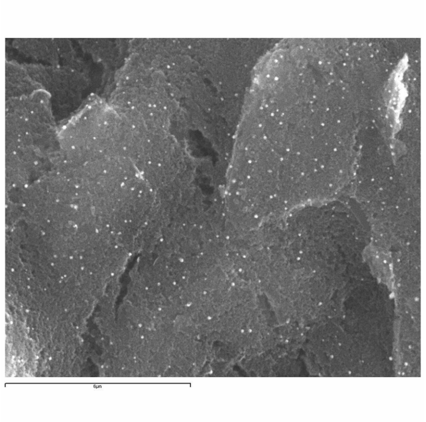

Fig. 1. **SEM image of the gold nanostructure used as transducer**

Following this methodology, SARS virus targets can be determined in a quantitative range from 5 pM to 100 pM. The use of these gold nanostructured surfaces improves the sensitivity obtained with continuous gold surfaces[2] with less consumption of reagents.

*This work has been supported by Spanish Project: BIO2006-15336-C04-01.*

REFERENCES

1. Fanjul-Bolado P., Hernández-Santos D., González-García M. B., Costa-García A.: Anal. Chem. *79*, 5272 (2007).
2. Abad-Valle P., Fernández-Abedul M. T., Costa-García A.: Biosens. Bioelectron. *20*, 2251 (2005).

## PP103

## SOFT-LANDED PROTEIN VOLTAMMETRY FOR REDOX PROTEIN CHARACTERIZATION

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Microperoxidase-11 (MP-11) was soft landed onto the gold surface of a screen printed electrode. Intact protein deposition was verified by time of flight secondary ion mass spectrometry (ToF-SIMS). The coupling of soft landing with electrochemical techniques allowed unique information to be obtained about the deposition features. A full characterization of the direct electron transfer properties was performed by modeling data obtained from cyclic voltammetry experiments; calculated values of kinetic electron transfer constant, formal redox potential allow us to hypothesize the mechanism involved in soft landing immobilization and demonstrate the different conformation of the enzyme deposited from two different charged species. The strong interaction between MP-11 and the gold surface and long-term stability of the functionalized electrode characterize the peculiar features of this procedure which enhance its power with respect to the existing immobilization procedure and ensure its suitability for those practical applications which could benefit from an unmediated bridgeless bioelectrochemical electron transfer.

*This project has been co-funded by the European Commission under contract number 017350 (BioMedNano).*

## PP104

## As(III) QUANTIFICATION BY SQUARE WAVE ANODIC STRIPPING VOLTAMMETRY AT A PLANAR SILVER ELECTRODE

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Arsenic is a toxic element which is known to be carcinogenic. Arsenic is found in a wide variety of chemical species throughout the environment and can be readily transformed by microorganisms, changes in geochemical conditions, and other environmental processes. While arsenic occurs naturally, it can be found as consequence of a variety of industrial applications, including leather and wood treatments, and pesticides.

Based on the fact that water consumption is the most important source for Arsenic poisoning, the World Health Organization has established 10 mg L$^{-1}$ as the provisional concentration guideline for total arsenic concentration in drinking water. Nevertheless, in many countries this concentration has been overcome, which is found to be related with adverse effects to population health[1].

Looking for a simple, affordable, sensitive and easy-to-implement quantification alternative for *in-situ* analysis of arsenic, diverse electrochemical methods based on anodic stripping voltammetry (ASV) have been recently reported. In spite of the great advantages of arsenic analysis by ASV, some disadvantages are distinguished, like the toxicity or the expensive cost of working electrodes (Hg, Au and Pt)[2].

In the present study an electrochemical assay for As(III) quantification using square wave anodic stripping voltammetry at silver screen-printed electrodes is presented. The planar strips demonstrate a good behavior even without stirring the plating solution during the deposition process and in presence of dissolved oxygen. The detection limit was 10 μg L$^{-1}$ and the linearity range from 19 to 300 μg L$^{-1}$. The effect of the most important ion interferences ($Cl^-$, $Hg^{2+}$, $Pb^{2+}$ and $Cu^{2+}$) on stripped signal is also described. The proposed electrodes demonstrated to be suitable for *in-situ* As(III) analysis.

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*29A UAEH PAI-2006 projects. S.P.M.C. and M.H.C. are grateful for their studentship granted by CONACyT. J A R., G.A.A.R., M.E.P.H. and C.A.G.V. also thank SNI (México) for the stipend received.*

REFERENCES

1. World Health Organization, 2001 Fact sheet No. 210. www.who.int/mediacentre/factsheets/fs210/en/ (2008 February).
2. Hung D., Nekrassova O., Compton R.: Talanta *64*, 269 (2004).

## PP105

## DETERMINATION OF GUANOSINE 5'-MONOPHOSPHATE BY SQUARE WAVE VOLTAMMETRY WITH A MODIFIED GOLD ELECTRODE

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The aim of the present work was the study of electrochemical behaviour and the subsequent determination of the nucleotide guanosine 5'-monophosphate (GMP) by square wave voltammetry (SW). For these studies a modified gold electrode was used. First, a modification with an organosulfhur compound was made, 1,2-ethanedithiol (EDT), which acted as a spacer and it spontaneously bonded to the surface of gold electrode (Au-EDT). Then, the electroactive surface of electrode was increased with gold nanoparticles (AuNPs), producing a spontaneously chemistry adsorption with the sulphur compound (Au-EDT-AuNPs). The formation and caracterization of the nanoparticles solution were realized by UV-VIS spectroscopy and an Atomic Force Microscopic (AFM). The complementary nucleotide of GMP with an atom of sulphur in its structure (4-amino-2-mercaptopirymidine, TC) was utilized for the detection and quantification of GMP; a spontaneous bond between complementary nucleotide and gold nanoparticles was formed, and the modification of gold electrode was finished. For successive studies the totally modified gold electrode was used and was denoted as Au-EDT-AuNPs-TC.

When the modification of electrode was optimized, the electrochemistry study and optimization of the conditions of measurement were realized for the direct determination of GMP by square wave voltammetry.

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## PP106

## $H_2O_2$ DETERMINATION AT IRON-RICH CLAY MODIFIED ELECTRODES

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Clay modified electrodes (CME) have been studied extensively because of the ion exchange properties of the clays, their layered structure and their chemical stability. The major constituents of most common smectite clays are aluminum and magnesium. But natural clays are never pure, they always contain small amount of other elements, i.e. iron. These trace elements can affect the response of CME with an electrocatalytic behavior. For instance, Oyama and Anson reported that structural iron sites could mediate the reduction of hydrogen peroxide[1]. However the proposed redox activity of iron in CME has always involved adsorbed electroactive species as charge mediators ($Ru(NH_3)_6^{2+}$, $Fe(bpy)_3^{3+}$, $MV^{2+}$)[2–3]. Electroluminescence experiments confirmed that iron species contained in the clays can mediate an electron transfer[4,5].

In this study, we investigated the electrochemical properties of several ferruginous clays, either natural or synthetic. Three different conditions have been tested at the CME for the reduction of $H_2O_2$:

a) in acidic medium without redox mediator,
b) in neutral medium (pH 8) with adsorbed $MV^{2+}$ as a charge shuttle,
c) in neutral medium (pH 7) with absorbed Hemoglobin as a biocatalyst.

The resulting CME were characterized by cyclic voltammetry in the presence or not of $H_2O_2$ and finally the calibration curves were recorded under amperometric conditions. The results will be discussed in relation to the clay properties, in particular the iron amount present in their structure and its structural sites.

*This work is supported by the CMCU (06/S1207) et MIRA 2007.*

REFERENCES

1. Oyama N., Anson F. C.: J. Electrochem. Chem. *199*, 467 (1986).
2. Zen J.-M., Jeng S.-H., Chen H.-J.: J. Electroanal. Chem. *408*, 157 (1996).
3. Xiang Y., Villemure G.: J. Electroanal. Chem. *382*, 21 (1995).
4. Ouyang C. S., Wang C. M.: J. Electrochem. Soc. *145*, 2654 (1998).
5. Teng Y.-W., Chang I.-Jy., Wang C. M.: J. Phys. Chem. *101*, 10386 (1997).

## PP107

## VOLTAMMETRIC DETERMINATION OF 2,4-DINITROPHENOL AT BORON-DOPED DIAMOND FILM ELECTRODE

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Boron doped diamond (BDD) is a novel and versatile electrode material, which has gained popularity in a variety of electrochemical applications[1,2]. BDD thin-film electrodes possess excellent electrochemical properties, such as extreme hardness, low and stable background current over a wide potential range, microstructural stability at extreme cathodic and anodic potentials, high current densities, good responsiveness for many redox analytes without pretreatment, and resistance to electrode fouling[3].

Nitrophenols coming from pesticide degradation, car exhausts, and industrial wastes are listed as priority pollutants by the US Environmental Protection Agency. They are considered to be potentially carcinogenic and mutagenic. Pesticides based on simple nitrophenols are used as growth stimulators in agriculture[4]. Moreover, 2,4-dinitrophenol (2,4-DNP) is a suitable model of nitrated explosives[5]. 2,4-DNP has been determined at BDD film electrode (Windsor Scientific, UK) by differential pulse voltammetry. The influence of pH at voltammetric behavior of 2,4-DNP was investigated using electrochemical reduction and oxidation in Britton-Robinson buffer over a pH range of 2–12. The concentration dependences were measured under optimum conditions. The voltammetric behavior of 2,4-DNP has been compared with 2-nitrophenol and 4-nitrophenol.

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REFERENCES

1. Chailapakul O., Siangproh W., Tryk D. A.: Sens. Lett. *4*, 99 (2006).
2. Fujishima A., Einaga Y., Rao T. N., Tryk D. A.: *Diamond Electrochemistry*. Elsevier, Amsterdam 2005.
3. Xu J. S., Chen Q. Y., Swain G. M.: Anal. Chem. *70*, 3146 (1998).
4. Fischer J., Barek J., Wang J.: Electroanalysis *18*, 195 (2006).
5. Zaleska A., Hupka J.: Waste Manage. Res. *17*, 220 (1999).

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## PP108

## POLYMER – IONIC LIQUID ELECTROLYTES FOR ELECTROCHEMICAL GAS SENSORS

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Room temperature ionic liquids attract the attention thanks to their excellent properties: non-volatility, high conductivity, liquidity in wide temperature range, high thermal stability (up to 400 °C) and low toxicity[1]. Especially for electrochemical gas sensors their high electrochemical stability is highly appreciated[2].

Our recent research is aimed at development of new binary systems polymer-ionic liquid serving as an electrolyte for electrochemical gas sensor for $NO_2$. Previously used electrolytes were usually ternary systems polymer-aprotic solvent-salt[3,4], while now is the function of embedded solution of salt in a solvent substituted with a hydrophobic ionic liquid based on 1-methylimidazole. We have combined several ionic liquids with various methacrylate polymers forming elastic, homogenous and long-term stable electrolytes.

### Experimental

Following monomers or macromonomers (2-hydroxyethyl methacrylate HEMA, poly(ethylene glycol) methacrylate PEGMA and poly(ethylene glycol) methyl ether methacrylate PEGMEMA – all from Sigma-Aldrich) and ionic liquids (1-butyl-3-methylimidazolium hexafluorophosphate $BMIPF_6$, 1-butyl-3-methylimidazolium tetrafluoroborate $BMIBF_4$ and 1-ethyl-3-methylimidazolium tetrafluoroborate $EMIBF_4$ – all prepared following literature[1,5,6]) were combined.

Polymer electrolytes were prepared by direct, thermally initiated radical polymerization (150 min at 80 °C) of the initial liquid mixture containing the monomer, ionic liquid and polymerization initiator (2,2'-azobis(isobutyronitrile). The polymerization was carried out in a cell formed of polypropylene plate, packing distance frame (silicone rubber) and glass plate.

Electrochemical characterization of prepared electrolytes was performed on a potentiogalvanostat PGSTAT 30 (Eco Chemie, The Netherlands) including the FRA-2 module for impedance measurements.

### Results and discussion

The first objective was to find chemically compatible pair of a monomer and a strongly polar ionic liquid. Therefore more polar monomers containing either -OH group and/or $(CH_2CH_2O)_n$ units in the structure were employed.

The combinations PEGMEMA-$BMIPF_6$ and PHEMA-$BMIBF_4$ form samples with suitable mechanical properties allowing both manipulation and electrochemical tests such as impedance and voltammetrical measurements.

Impedance measurements showed a reasonable ionic

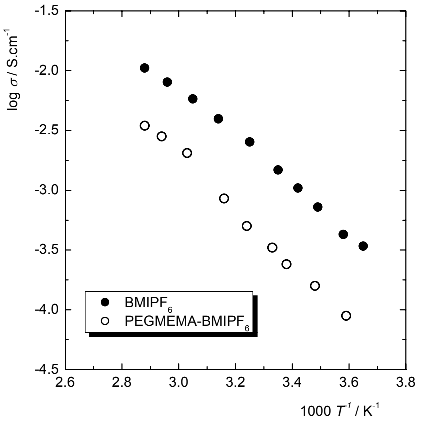

Fig. 1. **Dependency of conductivity on reciprocal temperature of PEGMEMA-BMIPF$_6$ electrolyte (43:57 mol.%) and neat BMIPF$_6$**

conductivity of PEGMEMA-BMIPF$_6$ electrolyte ($2.4\times10^{-4}$ S cm$^{-1}$ at 20 °C). Fig. 1 shows the relationship between conductivity and temperature of a polymer electrolyte and neat ionic liquid.

Voltammetrical measurements on a platinum electrode showed a broad accessible electrochemical window, especially in the case of electrolytes with PEGMEMA polymer. The absence of a hydroxyl group ensures the electrochemical stability from −2.3 to 2.5 V *vs.* Cd-Cd$^{2+}$ making the electrolytes perspective also for lithium-ion batteries.

Subsequently, the electrolytes characterized above will tested in an electrochemical sensor designed in previous research[3,4].

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REFERENCES

1. Bonhote P., Dias A. P., Papageorgiou N., Kalyanasundaram K., Gratzel M.: Inorg. Chem. *35*, 1168 (1996).
2. Ohno H. (ed.): *Electrochemical Aspects of Ionic Liquids*. John Wiley, NY 2005.
3. Hrnčířová P., Opekar F., Štulík K.: Sens. Actuators, B *69*, 199 (2000).
4. Hoherčáková Z., Opekar F.: Sens. Actuators, B *97*, 379 (2004).
5. Reiter J., Vondrák J., Michálek J., Mička Z.: Electrochim. Acta *52*, 1398 (2006).
6. Lewandowski A., Swiderska A.: Solid State Ionics *169*, 21 (2004).

## PP109

## ONE-STEP ENCAPSULATION OF BIOMOLECULES IN ELECTROGENERATED SOL-GEL FILMS FOR BIOSENSING APPLICATIONS

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Sol-gel electrochemistry has gained great popularity in the past decade, mostly because of the ease of formation of silica and organo-silica films with tailor-made properties that can be advantageously exploited for several applications when coated on a suitable electrode surface[1]. The usual way to get such films involves either dip- or spin-coating a sol-gel medium containing the appropriate (organo)alkoxysilane precursor(s), which are hydrolyzed and (co)condensed on the electrode surface. Such film-modified electrodes have found applications in various fields including electroanalysis and sensors, electrocatalysis, or bioelectrochemistry[1].

Some years ago, Shacham and co-workers have developed a new and elegant electrochemically-driven deposition method for getting sol-gel thin films on conducting substrates[2]. The approach is based on altering the surface pH by applying a suitable potential to an electrode immersed in a sol-gel medium, inducing thereby the catalysis of the condensation process thus enhancing the rate of film deposition[3,4].

This work points out that electrogeneration of silica gel films on glassy carbon electrodes can be applied to immobilize biomolecules – hemoglobin (Hb) or glucose oxidase (GOD) or both of them in mixture – without preventing their activity. These proteins were physically entrapped in the sol-gel material in the course of the electro-assisted deposition process applied to form the thin films onto the electrode surface. Successful immobilization of proteins was checked by various physicochemical techniques. Hb entrapped in the silica thin film displayed an electrocatalytic behavior towards $O_2$ and $H_2O_2$ in solution, respectively in the mM and µM concentration ranges. Immobilized GOD kept its biocatalytic properties towards glucose. Combined use of these two proteins in mixture has proven to be promising for detection of glucose in solution via the electrochemical monitoring of oxygen consumption (decrease of the oxygen electrocatalytic signal)[5].

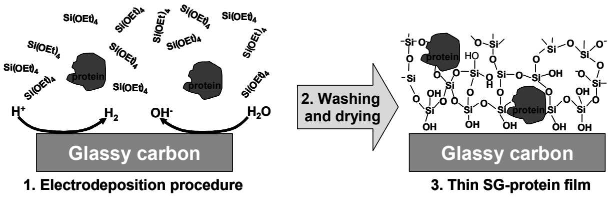

Fig. 1. **Electrogeneration of sol-gel films in the presence of proteins**

REFERENCES
1. Walcarius A., Mandler D., Cox J., Collinson M. M., Lev O.: J. Mater. Chem. *15*, 3663 (2005).
2. Shacham R., Avnir D., Mandler D.: Adv. Mater. *11*, 384 (1999).
3. Sayen S., Walcarius A.: Electrochem. Commun. *5*, 341 (2003).
4. Walcarius A., Sibottier E.: Electroanalysis *17*, 1716 (2005).
5. Nadzhafova O., Etienne M., Walcarius A.: Electrochem. Commun. *9*, 1189 (2007).

## PP110

## THE DETERMINATION OF DIFFUSION COEFFICIENT OF MONOSACHARIDS WITH ELECTROCHEMICAL MICROSCOPY

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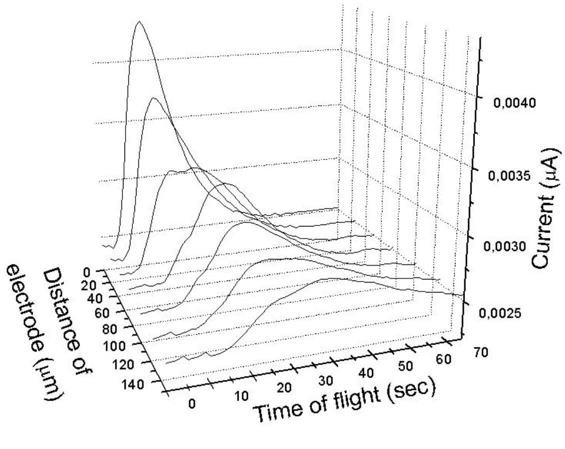
The diffusion coefficient of carbohydrates in different media is an important parameter in several areas. High numbers of methods are available for measuring it. Several of them use electrochemical detection.

A simple method, based on special capability of Scanning Electrochemical Microscopy (SECM) for the accurate measurement of diffusion coefficient has been worked out in our laboratory.

It is based on detecting the concentration – time transients with appropriate electrochemical micro-sensor positioned at the close vicinity of a miniature dose source device. At given time ($t_i$) a small dose of the investigated species is introduced. The $\Delta t_{max} = (t_{cmax}-t_i)$ value and the distance ($d = x + \Delta x_n$) between the source and the detector microelectrode are used for calculation of $D$. While the original set distance ($x$) can not be accurately measured in the micrometer scale, the tip travel distance ($\Delta x_n$) of the microscope is well defined. Collecting a few $\Delta t_{max} - (x + \Delta x_n)$ data pairs reliable value of the diffusion coefficient can be obtained. The procedure is simple and does not require knowing the dose size introduced.



In the work, to be presented the basic principle of the new method will be presented, and the values obtained with it will be compared with diffusion coefficient values obtained using conventional electrochemical methods. In the experiments micro size copper SECM tip, enzyme sensor, and conventional size electrodes were used. Diffusion coefficients of glucose arabinose and other monosaccharide were measured.

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REFERENCE
1. Csóka B., Nagy G.: J. Biochem. Biophys. Meth. *61*, 57 (2004).

## PP111

## BIOSENSORS AND ELECTROCHEMICAL DETECTION TECHNIQUES FOR CLINICAL DIAGNOSIS

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Recently a new measuring method has been worked out in our laboratory. The so called periodically interrupted amperometry (PIA) was proved very useful in lowering the detection limit of membrane coated electrodes, like amperometric biosensors.

As it is well known, the amperometric enzyme electrodes are made of a voltammetric base sensing element and different layers -among them enzyme containing reaction layer-coating its surface. In conventional amperometry the electrode potential kept constant, and the current generated by the electrode reaction is detected.

The concentration of electroactive species formed in the enzyme catalysed reaction is decreased by the continuous action of the electrode process. In this way the stationer layer at the surface of the sensing element gets more or less depleted.

It was expected, that periodic interruption of the electrolysis, would allow time for reloading the layer at the close vicinity of the sensing element. This could result in higher current and lower detection limit in case of an enzyme sensor.

In our presentation the basic principle of the PIA method will be introduced. In the experimental work to be presented glucose and putrescine measuring enzyme electrodes were prepared with three different stationary layers on their surface.

Platinum disc electrodes were used for preparation of the enzymatic working electrodes. PIA measuring program was applied and optimized, selecting the optimal measuring ($t_M$) and resting ($t_R$) time periods and the data collecting parameters.

Conventional amperometric detection and PIA detection were compared. The signals obtained with the optimized PIA program was much higher than the current obtained with the classical amperometry. Results show that the PIA detection extends the measurement range of membrane coated amperometric sensors. In clinical samples putrescine is in lower μM range. Therefore lowering the detection limit is an important step forward.

*The authors would like to thank Hungarian Scientific Research Found for financially supporting this research with grant T 037403 and T 049502.*

REFERENCES

1. Nagy G., Nagy L.: Anal. Lett. *40*, 3 (2007).
2. Nagy L., Kálmán N., Nagy G.: J. Biochem. Biophys. Meth. *69*, 133 (2006).
3. Nagy L., Nagy G., Gyurcsányi R. E., Neuman M. R, Lindner E.: J. Biochem. Biophys. Meth. *53*, 165 (2002).

## PP112
## CARBON PASTE ELECTRODE MODIFIED WITH COAL

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The electrochemical properties of coals have been mostly studied by means of measurement in the coal slurries in electrolytes[1]. Carbon paste electrode modified with carbonaceous materials (eg. activated carbon) has been also used for this purpose[2].

Carbon paste electrode (CPE) with mixed coal was prepared in order to find another possibility to investigate coals or carbonaceous materials. Samples of the used bituminous coal were from Ostrava-Karvina Coal Mines District. They were already characterized by proximate, ultimate as well as micropetrographic analyses.

The electrode was prepared by procedure similar to preparation of clay modified CPE[3]. The prepared electrodes were tested as to their mechanical properties and potential range in various electrolytes (acetate buffer pH 3,6, HCl, KCl, and NaOH (all 0,1 mol l$^{-1}$). The potential ranges of the coal modified electrodes were broader in all the tested electrolytes in comparison with the unmodified CPE, especially in the positive potential direction. Cyclic voltammetry of ion pair $[Fe(CN)_6]^{3-/4-}$ exhibited low current values. An influence of coal particle size on the electrochemical behaviour of the coal CPEs was studied, too.

Deposition of Hg film on the surface of the coal CPE showed possibility to use it either as a substrate for metals deposition or as a means for study of the sorption properties of coals.

*The work was supported by the Grant Project No. IAA301870801, Grant Agency of the Academy of Sciences of the Czech Republic.*

REFERENCES

1. Patil P., DeAbreu Y., M., Botte G. G.: J. Power Sources *158*, 368 (2005).
2. Kaplan J. D., Marsh J. H., Orchard S. W.: Electroanalysis *5*, 509 (1993).
3. Navratilova Z., Kula P.: Electroanalysis *15*, 837 (2003).

## PP113
## COMPOSITE BIOELECTRODES BASED ON LIPIDIC CUBIC PHASE WITH CARBON NANOTUBE NETWOK

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The important features of biofuel cell are the ability to convert chemical energy to electricity with high efficiency, at room temperatures and under conditions close to physiological. Monoolein liquid-crystalline films is a convenient matrix to immobilize biocatalysts at the electrode surfaces in their active form. The lipidic cubic phase can be characterised as a curved, non-intersecting bilayer with two unconnected water channels. Monoolein (MO) is an example of a lipid forming such a phase. It is highly viscous, transparent and at hydration over 20 % is stable in contact with water. Doping MO with 1,2-dioleoyl-sn-glycero-3-phosphate increases the shear strength of the $MO/H_2O$ cubic phase and makes the aqueous channels walls anionic allowing for more stable immobilization of cationic mediators inside the cubic phase due to electrostatic interactions. Using the monoolein cubic phase for hosting the enzymes allowed also to avoid any additional separating membranes in the biofuel cell, keeps the enzymes active and close to the electrode surface. In our membraneless biofuel cell (BFC) glucose oxidase and laccase were the anodic and cathodic catalyst, respectively, the bioanode was glassy carbon rod modified with the cubic phase containing glucose oxidase isolated from *Aspergillus niger* and tetrathiafulvalene (TTF), methylene green or ferrocenecarboxylic acid as the mediators. The biocathode was glassy carbon modified with the cubic phase and laccase from *Cerrena unicolor*. ABTS as the mediator was applied to this system. Such biofuel cell uses glucose as the anode fuel and dioxygen as the cathode fuel. We determined the main parameters of the presented biofuel cell. The open circuit potential V using TTF and ABTS mediators. was 450 mV The load in the range of 10 kΩ to 10 MΩ was applied to determine the cell current ($I_{cell}$) and the cell voltage ($V_{cell}$). The maximum power density was 7 μW cm$^{-2}$. To eliminate leaching of the mediators to the solution and improve current and power densities of the cell, selected mediators were bound covalently or adsorbed on single walled carbon nanotubes (SWNTs) forming a conductive network in the cubic phase film.

## PP114
## NOVEL TYPE OF SILVER AMALGAM PASTE ELECTRODE

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A new arrangement of silver amalgam paste electrode[1] (AgAPE) was developed for the voltammetric determination of 4-nitrophenol (4-NP). Due to easy surface renovation by simple procedure, the electrode was found to be useful for the determination of nitrated phenolic compounds in waste water. The electrode showed good reproducible results for 4-NP with relative standard deviation (RSD) 2.1 %. The reproducibility was also found good both in drinking water and river water with RSD 3.4 % and 4.8 %, respectively, without employing regeneration potential. The effect of electrode regeneration on peak current height was studied. The regeneration of electrode improved peak current stability with RSD 1.1 %. Under the optimized regeneration potential the peak current stability improved for 4-NP in drinking water but in river water it deteriorated which may be due to the presence of some other interfering substances. Some passivation has been observed for 2-methyl-4,6-dinitrophenol indicating that the passivation is connected with the properties of compounds. Furthermore, fairly good reproducibility (RSD lower than 10 %) of surface renovation has been observed. Under optimized condition the reduction peak currents were linear with the concentration of 4-NP from $4\times10^{-7}$ to $1\times10^{-4}$ mol $L^{-1}$with the correlation coefficient of R= 0.9997. The limit of determination for 4-NP at AgAPE was $3\times10^{-7}$ mol $L^{-1}$. The determination of 4-NP at AgAPE was carried out in model samples of drinking and river water and the limit of determinations were $2\times10^{-6}$ and $3\times10^{-6}$ mol $L^{-1}$, respectively.

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REFERENCE

1. Yosypchuk B., Šestáková I.: Electroanalysis *20*, 426 (2008).

## PP115
## NEW TYPES OF MINIATURIZED (MINI- TO NANO-VOLUME) ELECTRODES, CAPILLARY OR PLASTIC- TIP SENSORS AND PORTABLE SYSTEMS, BASED ON MERCURY, AMALGAMS, COMPOSITE OR PASTE AMALGAMS, ETC

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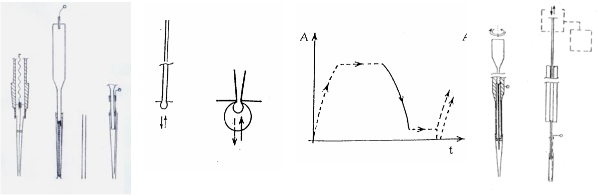
Sensors/electrodes based[5–9] on mercury, amalgams, solid or mercury modified amalgams, etc., occupy an important position among the working electrodes as to trace analysis[1–3] and study of bioactive species[4]. Recent development[5–9] of the mentioned stationary, renewed stationary or (time-dependent) controlled-size electrodes has brought suggestion of numerous new types of useful designs and applications concerning, e.g., the miniaturized electromechanically renewed hanging (stationary) mercury drop HMDE/SMDE electrodes[5,9], meniscus or hemisphere sensors, compressible/expansible electrodes[5,9], the sensors based on the mercury modified solid amalgams[7–9], composite or paste amalgams[6] and materials of the analogous consistence, capillary, plastic-tip[6], glass-tip[6] and other sensors as well as portable (or mobile) measuring systems[5]. New regimes, modes and applications based on analysis of physico-chemical factors and functioning conditions have been suggested. Now even the mini-, semimicro-, micro- or nanovolumes (nanoliters)[6] of the electrode phase can be used.



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REFERENCES

1. Barek J.: *Možnosti inovací v elektroanalytické chemii.* PACI (Eds: ESF; VŠCHT), Praha 2006.
2. Wang J.: *Analytical Electrochemistry.* VCH Publ., New York 1994.
3. Štulík K., Kalvoda R. (ed.): *Electrochemistry for Environmental Protection*. UNESCO ROSTE, Venice 1996.
4. Paleček E., Fojta M.: Anal. Chem. *73*, 74A (2001).
5. Novotný L.: Chem. Listy *95*, 147 (2001).
6. Novotný L.: Czech Patents, PUV 7103-1997; PV 1-2001; PUV 19501-2007, Prague.
7. Novotný L.,Yosypchuk B.: Chem. Listy *94*, 1118 (2000).
8. Yosypchuk B., Novotný L.: Crit. Rew. Anal. Chem. *32 (2)*, 141 (2002).
9. Novotný L.: Fresenius' J. Anal. Chem. *363*, 55 (1999).

## PP116
## NEW ELECTROANALYTICAL AND PHYSICO-CHEMICAL ASPECTS OF ELECTROCHEMICALLY RENEWED SENSORS BASED ON MERCURY OR AMALGAMS

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Use of purely mechanical renewal of the above-mentioned sensors (electrodes)[1–6] based on mercury or amalgams results in adequate consumption of the electrode phase, depending on the applied experimental conditions. The ways how to reduce a consumption of mercury or amalgams have been explored and tested. The obtained results outlined, that a combination of the mechanical and purely electrochemical renewal of the electrode surface of HMDE seems to be useful for many electroanalytical as well as physico-chemical applications. This finding is supported by the adequate physico-chemical reasons and interpretation of corresponding interfacial behavior of species present in the measured solution.

For example, application of purely electrochemically pretreated HMDE produced analogous sharp cathodic DPV-peaks of 2-aminoanhraquinine 2-AA in 0.05 M BrRo:MeOH 1:1, pH 4.6 at the same depolarization potentials as in the case of application of mechanically renewed HMDE resulting in $\Delta I$ *vs.* $c$ dependence of a parabolic shape exhibiting a more flat course approaching the linear dependence. It is so probably due to a time-dependent competition between adsorption of 2-AA and other multi-partical electrosorption interactions in the electrode boundary. There is a mixture of present physico-chemical (interfacial) processes influencing the actual state of the electrode surface. A reasonable sensitivity and reproducibility outlined a good analytical[1–6], biophysical[7], etc., applicability of the discussed electrochemical renewal.

*This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic (VZ 0021627502-UPa and LC06035).*

REFERENCES

1. Barek J.: *Možnosti inovací v elektroanalytické chemii.* PACI (ESF; VŠCHT, ed.), Praha 2006.
2. Wang J.: *Analytical Electrochemistry.* VCH Publ., New York 1994.
3. Štulík K., Kalvoda R. (ed.): *Electrochemistry for Environmental Protection.* UNESCO ROSTE, Venice 1996.
4. Novotný L.: Czech Patents, PUV 7103-1997; PV 1-2001; PUV 19501-2007, Prague.
5. Novotný L.,Yosypchuk B.: Chem. Listy *94*, 1118 (2000).
6. Yosypchuk B., Novotný L.: Crit. Rew. Anal. Chem. *32*, 141 (2002).
7. Paleček E., Fojta M.: Anal. Chem. *73*, 74A (2001).

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## PP117
## GRAPHITE FOILS AS WORKING ELECTRODE SOURCE IN AMPEROMETRIC FLOW INJECTION ANALYSIS OF PHARMACEUTICAL MOLECULES

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Graphite foils are widely used as a sealing material for high temperature, high-pressure transfer of liquids, gases, steam, chemicals and corrosives, as gaskets material in automotive, petroleum, chemical, paper, and nuclear industries, and as bipolar plates in the fuel cell industry.

A potential application almost unexplored of bare graphite foil is the development of electrochemical sensors, aiming analytical applications. Graphite foils were used as substrate for enzyme immobilization for the confection of biosensors[1], as electrode for fuel cell[2,3], and as substrate to grow carbon nanotubes[4].

Herein we describe the use of graphite foils as the working electrode in flow systems employing amperometric detection. In our studies, graphite foils were adapted in a flow cell and applied for the determination of pharmaceutical products.

Fig. 1 shows the electrochemical flow cell: It is constituted by two acrylic blocks (A), which are tighten by two screws (B). A polyethylene foil (C) containing a hole (G), which is positioned between the two blocks, over the graphite foil (D), used as working electrode. In the outlet channel of the cell, a stainless steel tube (E) works as the auxiliary electrode. Near to this tube, in the outgoing channel was positioned the miniaturized Ag/AgCl electrode (F). The arrows indicate the inlet and outlet of the solution. Polyethylene tubes are used to conduct the solution to the cell.

Prior to the electrochemical flow cell, there is an injection valve at which a sample loop with a fixed volume is injected in the flow system. The solution was propelled by the gravity force by placing a vessel containing electrolyte at 1 meter height and controlling the flow rate pinching a Tygon® tube which was inserted in the line.

Cyclic voltammetry was employed to investigate the

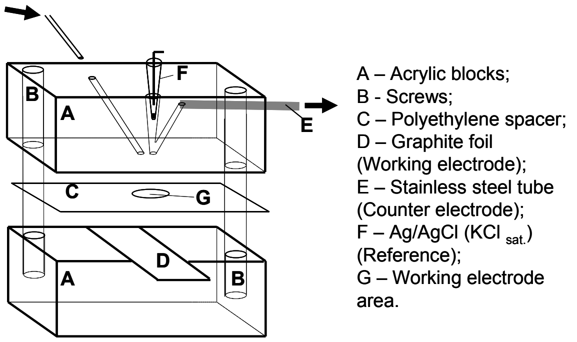

Fig. 1. **Electrochemical cell for flow injection analysis (FIA) constructed in our laboratory.** The arrows indicate the inlet and outlet of the carrier solution

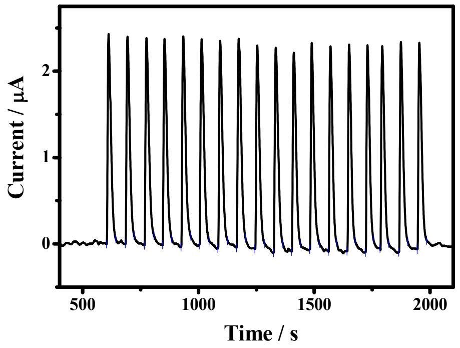

Fig. 2. **Amperometric responses for eighteen consecutive injections of $1\times10^{-4}$ mol $L^{-1}$ acetaminophen**

electrochemical oxidation of acetaminophen and ambroxol at graphite foil electrodes. The good performance for the alternative electrode allowed the use of amperometry in a FIA system. The first experiments were carried out to optimize the FIA system for the amperometric determination of acetaminophen.

The best conditions were +0.7 V as the working potential, flow rate of 2 mL $min^{-1}$, sample loop of 200 µL, and 0.1 mol $L^{-1}$ KCl as the supporting electrolyte. Fig. 2 shows the amperometric responses for eighteen consecutive injections of $1\times10^{-4}$ mol $L^{-1}$ acetaminophen under the optimized conditions. The relative standard deviation was 2.7 %.

These preliminary results show the potential application of graphite foils as electrochemical sensors for FIA systems. The advantages of using such material as electrode are its low cost, which would allow the production of disposable electrodes. The determination of ambroxol using the proposed analytical system is now been optimized. Graphite foil electrode may also be used as a substrate for electrodeposited catalysts to produce sensors with improved selectivity and sensibility.

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REFERENCES

1. Palleschi G., Turner A. P. F.: Anal. Chim. Acta *234*, 459 (1990).
2. Mathur R. B., Maheshwari P. H., Dhami T. L., Sharma R. K., Sharma C. P.: J. Pow. Sour. *161*, 790 (2006).
3. Zhang X., Shen Z.: Fuel *81*, 2199 (2002).
4. Villers D., Sun S. H., Serventi A. M., Dodelet J. P.: J. Phys. Chem. *110*, 1469 (2006).

## PP118

## STUDY OF THE ELECTROCHEMICAL PROPERTIES OF RIGID COMPOSITES ELECTRODES AS A FUNCTION OF THEIR MWNT CONTENT

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Carbon nanotubes (CNT) have been attracting considerable attentions over the last decade due to their remarkable mechanical and electrical properties[1]. CNTs have a novel structure, highly accessible surface area, low resistance, and high stability. It has been experimentally shown that composites based on the combination of CNT with a insulating matrix improve the electric conductivity as well as the mechanical properties of the original polymeric matrix[2,3]. The transition from an insulating to a conducting composite is a function of the CNT loading. When a first network is developed throughout the insulating matrix, the composite resistivity lowers by several orders of magnitude. When this drop occurs, it is called percolation threshold. Although the variation of the mechanical and electrical properties of composite containing different CNT percentages, has been investigated and evaluated by other authors[4,5], their influence in the electrochemical properties of composites has not received the same attention..

The aim of the present study is to optimise the CNTs loading in the insulating matrix (resin epoxy) by means of electrical and morphological measurements and then to determine how the electrical properties affect the analytical response of the composites when they are used as amperometric sensors.

The multiwall carbon nanotubes used in this study (MWNT, purity > 95 %, length 5–15 µm, OD 10–30 nm) were supplied by SES Research (USA). The polymer matrix consisted of Epotek H77 with its corresponding hardener (Epoxy Technology, USA).

Previously to the fabrication of different composites, the MWNTs were pre-treated with nitric acid ($HNO_3$) for improving their homogenization. Composites with different MWNT loading were tested through the evaluation of their electrical, morphological and electrochemical properties.

REFERENCES

1. Chaudhary V. A., Mulla I. S., Sainkar S. R., Belhekar A. A., Vijayamohanan K.: Sens. Actuators, A *65*, 197 (1998).
2. Khare R., Bose S., Miner J.: Mater. Charact. Eng. *4*, 31 (2005).
3. Li H., Zhou Y., He B., Zhou W., Huang J., Li X., Wu B.: Electrochim. Acta *49*, 257 (2004).
4. Allaoui A., Bai S., Cheng H. M., Bai J. B.: Comp. Sci. Technol. *62*, 1993 (2002).
5. Kovacs J. Z., Velagara B. S., Schulte K., Bauhofer W.: Comp. Sci. Tech. *67*, 922 (2007).

## PP119

## A VOLTAMMETRIC APPROACH BASED ON THE USE OF PLATINUM MICROELECTRODES COUPLED WITH PRINCIPAL COMPONENT ANALYSIS FOR THE DISCRIMINATION OF OLIVE OILS

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In recent years, the use of analytical aspecific signals coupled with chemometric pattern recognition methods have found increasing applications for recognizing and discriminating liquid foods on the basis, for instance, of their geographical origin or manufacturing processes[1]. To this purpose, a variety of instrumental devices, so called electronic tongues, embracing mass, optical and electrochemical sensors have been proposed. As for the electrochemical systems, the most widely used are based on potentiometric, conductometric and voltammetric methods. The last techniques are particularly advantageous, because of their high selectivity, sensitivity, signal-to-noise ratio as well as for their various modes of measurements. With these systems, the use of bare metallic, carbon paste and chemically modified working electrodes of conventional size (*i.e.* millimeter dimension) have been so far mainly reported in the literature[1,2]. However, most applications have been concerned with high water content media, such as mineral waters, fruit juice and wines, which offer sufficient high conductivity to allow direct voltammetric measurements.

Direct applications of voltammetric electronic tongues in matrices characterised by high viscosity, low conductivity and unable to solubilise amounts of standard electrolytes, are instead rare. Food samples such as olive and in general vegetable oils are for instance practically inaccessible to voltammetric measurements, unless they are mixed with aqueous solutions and surfactants able to provide emulsified media. Another approach, recently proposed in the literature to solve these problems and to obtain suitable responses for chemometric treatments, has been the use of carbon paste electrodes modified with the oil sample analysed[3].

In this paper we propose an alternative "electronic tongue" based on Pt disk microelectrodes coupled with the Principal component Analysis (PCA) chemometric method[4], to differentiate vegetable oils according to their quality and geographical origin. The method is based on direct voltammetric measurements made in the oil sample mixed with a suitable room temperature ionic liquid (RTIL), added as supporting electrolyte to make the matrix conductive enough. The optimal oil-to-RTIL mixture composition and cyclic voltammetric parameters are preliminarily investigated. The effect of trihexyl(tetradecyl) phosphonium decanoate (TETDP) is in particular tested here, and the voltammetric results obtained in such experimental conditions are presented. From data analysis performed *via* PCA, the usefulness of the complete current/potential responses, considered as a "fingerprint" of the samples, to discriminate among different oils is finally discussed.

REFERENCES

1. Ciosek P., Wroblewski W.: Analyst *132*, 963 (2007).
2. Martina V., Ionescu K., Pigani L., Terzi F., Ulrici A., Zanardi C., Seeber R.: Anal. Bioanal. Chem. *387*, 2101 (2007).
3. Apetrei C., Rodriguez-Mendez M. L., de Saja J. A.: Sens. Actuators, B *111-112*, 403 (2005).
4. Forina M., Lanteri S., Casolino C., in: *Handbook of Food Analysis*, Vol. 3, p. 1757. Marcel Dekker, NY 2004.

## PP120

## A FLOW SYSTEM FOR UREA AND GLUCOSE MEASURMENT WITH A SELF POLISHING ELECTRONIC TONGUE

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A temporary flow system connected to a self polishing pulse voltammetric electronic tongue was evaluated for prediction of small changes in urea and glucose concentrations in phosphate buffer. Two batches of samples standards were used; one for calibration and the other for validation. The adhoc system could easily predict changes at around 10mg/l for both urea and glucose. No significant difference between the two batches was seen.

The flow system, were built from a set computer controlled sample valves in series with the self polishing electronic tongue and peristaltic pump. The voltammetric electronic tongue[1] used consisted of two working electrodes of gold and platinum, connected to an ISKRA MA5410 potentiostat controlled by a computer via an in lab built relay box. The housing of the electronic tongue was used as both counter and reference electrode. Currents from voltammetric pulses from 0 to ±1.3 V were recorded and further analyzed by PLS[2] under Matlab®. The self polish devise consist of a magnet that presses a rotating disc covered with grit paper on the

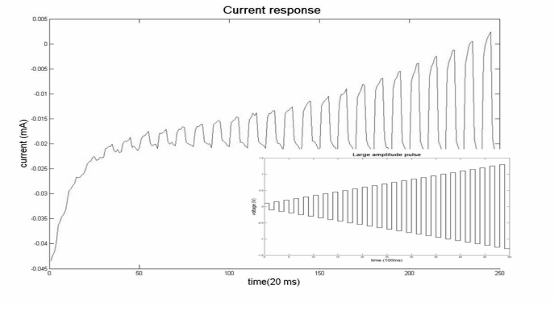

Fig. 1. **Typical stimuli and current response**

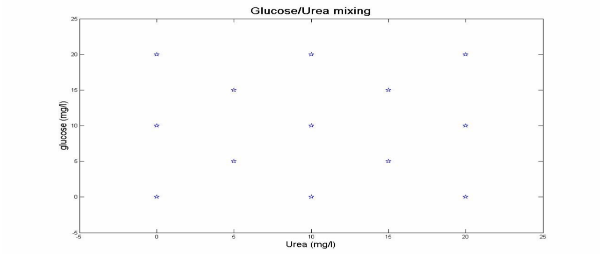

Fig. 2. **Mixing scheme**

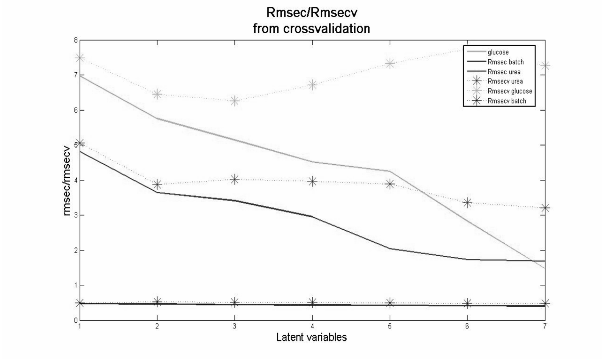

Fig. 3. **Rectified mean square error of calibration and validation *vs*. latent variables**

surface of the electrodes, this was also controlled by the computer[3].

Batches of samples was prepared using two buffer solutions of phosphate buffer (100 mM at pH~7) and different concentrations of both glucose and urea. Samples were analyzed in random order to eliminate time dependency in the calibration model.

The results show even if there are background levels of both glucose and urea changes, it is still possible to predict. Figure 3 showing calibration and validation error of the model with increasing number of latent variables, error of validation is about 7 and 4 mg/l for glucose respective urea. However these numbers can be decreased even further, using better laboratory practice and extracting key parameters from the signals. One of the main concerns was to eliminate the effect of different batch of buffers for the validation samples, this was confirmed by trying to predict the samples batch, this is seen in the figure 3, rmsec/rmsev for the batch prediction is fairly constant at 0.5 for up to seven latent variables.

Conclusions: The electronic tongue shows capability to monitor small changes in urea and glucose concentrations, further experiments will include physiological levels of both glucose and urea, also would the use of dialysis liquids be tested. Maybe the electronic tongue can be used for hemodialysis control.

REFERENCES

1. Winquist F., Wide P., Lundström I.: Anal. Chim. Acta *357*, 21 (1997).
2. Geladi P., Kowalski B.: Anal. Chim. Acta *185*, 1 (1986).
3. Olsson J., Winquist F., Lundström I.: Sens. Actuators *118*, 461 (2006).

## PP121

## CONTINUOUS MONITORING OF HEAVY METALS IN GROUNDWATER AS A TOOL FOR THE DETECTION AND VERIFICATION OF EARTHQUAKES

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Development of an automatic trace metal system (ATMS) has provided an opportunity to monitor earthquake precursor in basaltic rocks. Earthquake is a phenomenon which affects the lives of people at a lot of places all over the world. In areas with high earthquake activity new earthquakes can occur at any time – often with severe material damage and even loss of human lives.

Increased concentrations of some heavy metals in groundwater have been reported before an earthquake[1]. These anomalies were not detected until after the earthquake had occurred, because heavy metal concentrations were measured in the laboratory. In this study, we show how this limitation can be overcome using the ATMS. The ATMS uses different modes of voltammetry in combination with innovative solid alloy electrodes for real time monitoring of heavy metal concentrations[2,3].

In November 2006, an $M_W$ 4.5 earthquake occurred in Húsavík (Iceland). Continuous measurements showed visible changes in pH and electrolabile amounts of zinc, iron and copper 7–8 days before the earthquake. No metals were visible 30 days before the earthquake, but several metals were detected in the groundwater sample from 7 and 8 days before the earthquake, until the earthquake occurred. The results clearly show changes in the groundwater prior to an earthquake, which is possible to monitor with the ATMS.

REFERENCES

1. Claesson L.: Geol. Soc. Am. *32*, 641 (2004).
2. Mikkelsen Ø.: Electroanalysis *19*, 2085 (2007).
3. Mikkelsen Ø., Schrøder K. H.: Analyst *125*, 2163 (2000).

## PP122

# AMPEROMETRIC (BIO)SENSOR TRANSDUCERS BASED ON CARBON NANOTUBE MICROELECTRODE ARRAYS (UMAS)

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The discovery of the unusual properties of the ultramicroelectrodes in the eighties has opened new electrochemical and analytical possibilities, and new schemes of detection that are not possible with conventional electrodes[1]. Basically this electrodes exhibit very fast response, very high signal to noise ratio, and with the added non linear mass transfer features, very low limits of detection; all of these properties are highly desired in amperometric sensors. A way to maintain the electroanalytical advantages of the individual ultramicroelectrodes but with a response of amplified current can be obtained by means of arrays of ultramicroelectrodes (UMAs). Therefore, one of the big challenges in this area is the preparation and production of these ultramicroelectrodes.

Aside from the typical materials that can be used as transducer materials, it turns out to be very interesting the possibility to combine the properties of the UMAs with the exceptional properties of the carbon nanotubes (CNTs). They constitute the mechanically more strong structures[2] known up to now and exhibit great wealth in their electronic properties, from a semiconductor behaviour up to a metallic one[3]. On the other hand, they exhibit a great chemically/thermal stability, and constitute a strong base for the (bio)chemical functionalization[4] which favour them to be used as (bio)electrochemical sensors.

Hence, our main purpose is to search and design amperometric (bio)sensors based on CNT arrays and geometric configurations that improve the selectivity towards the analyte, that confer high sensitivity, fast response and that at the same time help to understand more deeply the physicochemical processes involved in such sensing phenomena.

These ultramicroelectrode arrays will be presented as the basis for the design of (bio)sensors for which different (bio) molecule immobilization techniques will be performed. We will resort to simple skills and to low cost chemical methods combining self- assembly and controlled CVD growrh of CNTs

## REFERENCES

1. Heinze J.: Angew. Chem. Int. Ed. Engl. *32*, 1268 (1993); Arrigan D. W. M.: Analyst *129*, 1157 (2004).
2. Dresselhaus M. S., Dresselhaus G., Avouris P.: *Carbon Nanotubes*. (Springer, Berlin 2001); Yu M.-F., Files B. S., Arepalli S., Ruoff R. S.: Phys. Rev. Lett. *84*, 5552 (2000).
3. Ding F., Bolton K., Rosén A.: J. Vac. Sci. Technol., A *22*, 1471 (2004).
4. Chen R. J., Zang Y., Wang D., Dai H.: J. Am. Chem. Soc. *123*, 3838 (2001).

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## PP123

# THE TIME-DEPENDENT POTENTIOMETRIC RESPONSE OF $Na^+$ SENSITIVE POLYMERIC MEMBRANES TREATED BY THE DLM AND NPP MODELS

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The membrane potential formation at ion-selective electrodes (ISEs) depends on the thermodynamic and kinetic properties of the membrane | solution system and strongly depends on time. For the theoretical modeling of the potentiometric signal several models can be applied[1]. The juxtaposition of theoretical potentiometric response with experimental data is shown.

For this purpose, the conventional construction of ISE with two types of polymeric membranes, that include different plasticisers *ortho*-nitrophenyl octyl ether (*o*-NPOE) and di (2-ethylhexyl) sebacate (DOS) ware applied.

The sodium sensitive PVC membranes were used to study the transient potential changes provoked by changing the concentration of potassium and lithium ions in the bathing solution. The transitory potential responses were observed for these ions and explained by the diffusion-layer model (DLM) and Nernst-Planck-Poisson model (NPP).

DLM model is based on the assumption of local equilibrium at the solution | membrane interface and NPP model allows for the interpretation of ISE response without assumptions about steady state and electroneutrality.

*This work was supported by the Polish Ministry of Science and Higher Education, Grant No. DWM/232/MATERA/2006.*

## REFERENCE

1. Bobacka J., Ivaska A., Lewenstam A.: Chem. Rev. (Review) *108*, 329 (2008).

### PP124

## APPLICATION OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY COUPLED WITH POTENTIOMETRIC METHOD AS TOOL IN OPTIMIZATION PARAMETERS OF ION-SELECTIVE ELECTRODES

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The influence of composition polymeric membranes on the ion transfer resistance at the aqueous solution and ion-selective membrane interface has been studied by potentiometry and electrochemical impedance spectroscopy (EIS).

It is well known that electrode properties such as selectivity against interferents, lifetime, and electrical behavior are determined by the composition of the ion-selective membranes. The conventional construction of potassium selective electrodes with typical composition of polymeric membrane used in experiments was divided into two groups. In the first one, nonpolar di(2-ethylhexyl) sebacate (DOS) was acted as the organic solvent and in the second one polar *ortho*-nitrophenyl octyl ether (*o*-NPOE). Each group was represented by three membranes with different among of ionophore. All membranes contained of potassium tetrakis (4-chlorophenyl) borate as an anion excluder.

Such membranes were tested in the solution including special selected ions (potassium, sodium and lithium) characterized by different mobility and energy of hydration. The changes in the potentiometric response and impedance spectra during conditioning in solutions mentioned above were monitored. Depends on hydrophilic degree of plasticiser and mobilities of ions different results have been observed.

*This work was supported by the Polish Ministry of Science and Higher Education, Grant No. DWM/232/MATERA/2006.*

### PP125

## MEMBRANE ELECTRODES FOR THE DIRECT AND MEDIATED ELECTROCHEMISTRY OF ENZYMES

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The use of membrane electrodes (ME), with the protein imprisoned between a dialysis membrane and the electrode surface, has some important advantages[1,2] and is an interesting strategy when adsorption of a protein or an enzyme onto the electrode surface is not successfully achieved, hindering the use of protein film voltammetry.

Our aim with this work is to compare the results obtained with metalloproteins in bulk and membrane entrapped solutions in order to gain a better insight into the interactions that occur at the membrane electrode surface and to highlight the effects of this strategy on the direct and mediated electrochemistry of metalloproteins.

This work reports the first electrochemical study of the electron transfer between a bacterial cytochrome *c* peroxidase (BCCP) and horse heart cytochrome *c*[3]. The mediated catalysis of BCCP from *Paracoccus pantotrophus* (Pp) was analysed using both strategies. The influence of parameters such as pH or ionic strength on the mediated catalytic activity was analysed using this approach, drawing attention to the fact that careful analysis of the results is needed to ensure that no artefacts are introduced by the use of the membrane configuration and/or promoters, and therefore the dependence truly reflects the influence of these parameters on the (mediated) catalysis.

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REFERENCES

1. Haladjian J., Bianco P., Nunzi F., Bruschi M.: Anal. Chim. Acta *289*, 15 (1994).
2. Correia dos Santos M., Paes de Sousa P., Simões Gonçalves L., Krippahl L., Moura J., Lojou E., Bianco P.: J. Electroanal. Chem. *541*, 153 (2003).
3. Paes de Sousa P., Pauleta S., Rodrigues D, Simões Gonçalves L., Pettigrew G., Moura I., Moura J., Correia dos Santos M.: J. Biol. Inorg. Chem., accepted.

### PP126

## AMPEROMETRIC IMMUNOSENSOR FOR THE DETERMINATION OF ANTI-*Clostridium tetani* ANTIBODIES

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An amperometric immunosensor for the determination of anti-*Clostridium tetani* antibodies in serum was developed. The methodology consists to perform the immunoaffinity reaction on magnetic beads in Eppendorf tubes and subsequently trap the resulting immunobeads onto a magnetized electrode for electrochemical sensing.

The tetanus toxoid antigen was immobilized on sub-

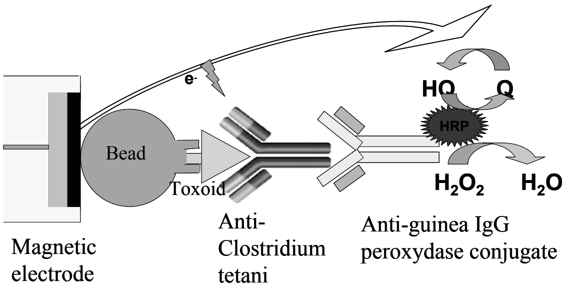

Fig. 1. **Schematic illustration of the amperometric-immunosensor**

micrometer size superparamagnetic beads. The use of the latter allowed for high efficiency of the immunological reaction. Different parameters affecting the immobilization of the tetanus toxoid onto the microbead surface were investigated. The toxoid antigen was biotinyled before its immobilisation onto the streptavidin precoated magnetic microparticles. Blocking of residual and unspecific binding sites was performed with bovine serum albumin.

The quantification of anti-tetani antibodies was accomplished by incubating the “bioactivated” microbeads with a solution of said antibodies followed by another incubation step with a peroxydase-labeled anti-IgG. Each incubation was followed by a washing step. After each incubation or washing step, the magnetic beads were separated from the supernatant by putting the tubes in a magnet separator. The microbeads were spiked onto a magnetized carbon paste electrode or a magnetized screen-printed carbon electrode for electrochemical detection in the presence of hydrogen peroxide and hydroquinone (HQ) as the redox label. The amperometric reduction current was studied, as a function of reaction time, in the presence of hydrogen peroxide and HQ.

## PP127

## THE USE OF BORON-DOPED DIAMOND FILM ELECTRODE FOR HPLC-ED DETERMINATION OF AMINOBIPHENYLS IN WATER SAMPLES

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Amino derivatives of biphenyl are suspected mutagens and/or carcinogens, 4-aminobiphenyl has been considered as human carcinogen since 1972 (ref.[1]). These compounds are emitted into the atmosphere by combustion of fossil fuels, they may be also present in cigarette smoke or hair dyes. Thus they are widely monitored in the environment as well as in biological liquids. Electrochemical detection using advanced electrode materials such as boron doped diamond thin films (BDDF)[2] offers sensitive and relatively selective tool for their determination as demonstrated for voltammetric methods[3].

This study is devoted to HPLC determination of 2-aminobiphenyl, 3-aminobiphenyl, and 4-aminobiphenyl in model samples of drinking and river water using amperometric detection in a thin layer cell with BDDF electrode. Satisfactory separation of studied analytes was achieved at a ChiraDex column with chemically bonded β-cyclodextrin in 0.001 M acetate buffer (pH 5):acetonitrile:methanole (40:30:30) mobile phase with total analysis time of six minutes. For direct determination of analytes in drinking and river water model samples limits of determination ~ $4\times10^{-7}$ M for all studied analytes were achieved, which is comparable to detection limits obtained under optimized conditions. Off-line solid phase extraction was further employed for preliminary separation and preconcentration of studied aminobiphenyls. Several extraction methods using Lichrolut EN® (Merck, Germany) cartridges were tested, including elution of the analytes with a mixture of methanole:acetonitrile:acetone (50:50:1, v/v/v; extraction efficiency ~ 70 %) or 0.01 M phosphate buffer:acetonitrile (50:50; extraction efficiency ~ 90 %). Elution with diethyl ether followed by its evaporation and reconstitution of the extract resulted in determination limits in the $10^{-8}$ M concentration range.

*K. P. thanks to the Grant Agency of the Czech Republic (grant 203/07/P261), the project was further financially supported by the Czech Ministry of Education, Youth and Sports (projects LC 06035 a MSM 0021620857).*

REFERENCES

1. IARC: *An Updating of IARC Monographs Volumes 1 to 42. Supplement 7.* IARC, Geneva 1987.
2. Fujishima A., Einaga Y., Rao T. N., Tryk D. A.: *Diamond Electrochemistry*. Elsevier, Amsterdam 2005.
3. Barek J., Jandová K., Pecková K., Zima J.: Talanta *74*, 421 (2007).

## PP128

## DESIGN AND DEVELOPMENT OF CARBON NANOTUBES / POLY-3-METHYLTHIOPHENE / LACTATE DEHYDROGENASE BASED BIOSENSORS FOR LACTATE DETERMINATION IN CHILEAN RED WINES

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Carbon nanotubes (CNTs) have characteristics for the development of electrochemical sensors by its unique physical properties such as conductivity and electrocatalytical effects[1]. In addition, poly-3-methythiophene (P3MT) is a conducting polymer widely used for minimization of the electrode fouling phenomena[2]. However, the association between these two materials has not being used simultaneously in biosensor design. Previously, we published an investigation about design and preparation of electrode surfaces based on modifications of CNTs with P3MT. Developed electrodes under these conditions show adequate electrochemical responses from various important molecules involved in metabolic pathways, such as NADH, FAD or cytochrome C (ref.[3]).

In this work, we studied different electrode surfaces (Pt, Au, GCE) modified with multi walled CNTs and P3MT for lactate biosensor design. Lactate dehydrogenase was used as biological recognition molecule and several immobilization strategies onto electrodic surface were achieved (adsorption, crosslinking). Lactate dehydrogenase catalyzed the following reaction:

Lactate + NAD = Pyruvate + NADH

Thus, NADH generated can be quantified by direct amperometry to an adequate potential depending on the electrode characteristics. The effect of pH, CNTS mass, number of electropolymerization cycles, concentration and type of supporting electrolyte were studied by different electrochemical techniques (CV, DPV).

Developed biosensors show good analytical performances, as well as a long term stability and low level of interferences. They were used for lactate determination in chilean red wines and thus to study the malo-lactic fermentation processes.

*Financial support from Fondecyt, CHILE (Research Project 11070056) is gratefully acknowledged.*

REFERENCES

1. Wang J.: Electroanalysis *17*, 7 (2005).
2. Luo X., Killard A. J., Morrin A., Smyth M. R.: Anal. Chim. Acta *575*, 39 (2006).
3. Agüí L., Peña-Farfal C., Yáñez-Sedeño P., Pingarrón J. M.: Electrochim. Acta *52*, 7946 (2007).

## PP129

## CHARACTERIZATION OF DIFFERENT URANIUM COMPOUNDS IN RELATION WITH THE NUCLEAR SPENT FUEL STORAGE USING VOLTAMMETRY OF MICROPARTICLES

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The environmental assessment of spent-fuel disposal requires the prediction of the release rates of radionuclides from the fuel if waste containers fail and the fuel comes into contact with ground water. Although the spent-fuel (mainly $UO_2$) is virtually insoluble in reducing media, its solubility increases dramatically under oxidizing conditions. Indeed, the water radiolysis – as a result of the $H_2O$ irradiation by the nuclear fuel – leads to the formation of oxidizing species, as $H_2O_2$, therefore U(IV) is transformed into soluble U(VI)[1]. Today different host matrixes are envisaged to avoid the dissemination of radioactive wastes in the environment. The thorium phosphate-diphosphate (TPD), $Th_4(PO_4)_2P_2O_7$, displays interesting properties as a potential host matrix because the TPD structure can incorporate uranium by substitution of $Th^{4+}$ ions by $U^{4+}$ ions with formation of $Th_{4-x}U_x(PO_4)_2P_2O_7$ (TUPD)[2,3].

We used Voltammetry of MicroParticles[4] (VMP) – associated with *in situ* or *ex situ* Raman measurements – in order to evaluate the oxidizability of different U(IV) compounds and for characterizing some U(VI) ones in relation with the spent fuel storage. Therefore, our investigations allowed to spectrometrically identify the $UO_2$ electrooxidation products, to monitor the formation of uranyl peroxide ($UO_2O_2$), to demonstrate the decrease of the U(IV) oxidizability when inserted in the TPD matrix and to determine the uranium oxidation states in natural minerals such as $U(SiO_4)_{1-x}(OH)_{4x}$ (coffinite) and $Ca(UO_2)2SiO_3(OH)_2{\cdot}5$ $(H_2O)$ (uranophane) that that could play a determinant role during the underground deep storage of radioactive waste.

*This work was partially supported by the French Research Group NOMADE (GdR 2023).*

REFERENCES

1. Shoesmith D. W., Sunder S., Hocking W. H., in: *Electrochemistry of Novel Materials, Electrochemistry of $UO_2$ Nuclear Fuel*, (Lipkowski J., Ross P. N., ed.), Chap. 6, p. 297. VCH Publishers, New York 1994.
2. Dacheux N., Clavier N., Ritt J.: J. Nucl. Mater. *349*, 291 (1997).
3. Clavier N., du Fou de Kerdaniel E., Dacheux N., Le Coustumer P., Drot R., Ravaux J., Simoni E.: J. Nucl. Mater. *349*, 304 (1997).
4. Scholz F, Meyer B., in: *Electroanalytical Chemistry, A Series of Advances*, (Bard A. J., Rubinstein I., ed.), Vol. 20, p. 1. Marcel Dekker, New York 1998.

## PP130

## CHARACTERIZATION OF MWCNT/PS/ANTIBODY MEMBRANE PREPARED BY PHASE INVERSION AND ITS APPLICATION AS IMMNUNOSENSORS

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Recent advances in nanoscience greatly influence in the field of electrochemical biosensors during the past years. This has carried an important development of new bio-compatible and highly conductive materials for biosensing applications.

The combination of multi-walled carbon nanotubes (MWCNT) as transducer with polysulfone (PSf) polymer offers unique properties for the easy incorporation of biological moieties providing a composite with high electrochemical response to corresponding analytes.

In the phase inversion technique[1], a thin film of polymer solution is deposited on an inert substrate and then immersed into a coagulant bath containing a non-solvent with respect to

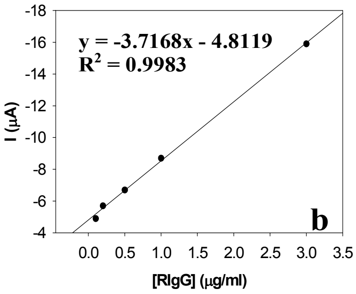

Fig. 1. **The current was monitored amperometrically at –0.225 V *vs.* S.C.E. and this method showed a linear range of the RIgG from 0.1 to 3 μg ml$^{-1}$**

the polymer, rapid exchange of the solvent by non-solvent results in diffusion-induced phase separation and membrane formation[2].

Confocal Scanning Laser Microscopy (CSLM) is a rapidly advancing imaging technique which obtains high-resolution images of membranes at successive depths, therefore offers a 3D view of membrane. Other techniques as X-Ray Powder Diffraction, Scanning Electron Microscopy (SEM) or Infrared Spectroscopy have completed the study of characterization of this composite membrane.

Finally, we have developed an immunosensor for a system of Ab model using peroxidase as enzymatic label and hydroquinone as mediator. Amperometric and voltammetric characterization is also made for the biosensing application.

*Acknowledgement: UAB P.I.F. fellow.*

REFERENCES

1. Zhang M., Gorski W.: J. Am. Chem. Soc. *127*, 2058 (2005).
2. Mulder M.: Kluwer Academia Publishers, (2000); Sánchez S., Fàbregas E.: Biosens. Bioelectron. *22*, 965 (2007).

## PP131

## DETERMINATION OF TRACE AMOUNT OF CADMIUM BY STRIPPING VOLTAMMETRY USING PAN-INCORPORATED NAFION MODIFIED GLASSY CARBON ELECTRODE

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A method for the trace determination of Cd(II), using a isposable 1-(2-pyridylazo)-2-naphthol (PAN)-Nafion coated modified glassy carbon electrode, has been developed. The modified electrode exhibited a significantly increased sensitivity and selectivity for Cd(II) while compared with a bare glassy carbon electrode (GCE). Cadmium ion (Cd2+) in 0.05 M potassium hydrogen phthalate (KHP) buffer is accumulated on the PAN-Nafion surface by the formation of a chemical complex at open circuit. GCE with complex Cd2+ is then transferred to 0.1 M KI and subjected to differential pulse anodic stripping voltammetry. Affected parameters were optimized to yield most suitable conditions with respect to the pH and concentration of accumulation medium, deposition potential, deposition time and volume of coated PAN-Nafion. The method has been successfully applied to the determination of Cd (II) in natural waste water.

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REFERENCES

1. Hart J. P., Wring S. A..: Trends Anal. Chem. *16*, 89 (1997).
2. Wang Z., Zhang H., Zhou S.: Talanta *44*, 621 (1997).
3. Hu Z., Seliskar C. J., Heineman W. R..: Anal. Chim. Acta *369*, 93 (1998).
4. Honeychurch K. C., Hart J. P., Cowell D. C..: Anal. Chim. Acta *431*, 89 (2001).
5. Wang Z., Zhang H., Zhou S., Dong W.: Talanta *53*, 1133 (2001).

## PP132

## AMPEROMETRIC DETECTION OF 4-CHLOROPHENOL ON TWO TYPES OF EXPANDED GRAPHITE BASED COMPOSITE ELECTRODES

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Zeolite-modified electrodes (ZMEs) have received attention in the development of electrochemical sensors[1–6]. In this work, the amperometric detection of 4-chlorophenol was investigated by cyclic voltammetry and linear-scan voltammetry using two types of composite electrodes, *i.e.*, expanded graphite-epoxy and Ag-doped zeolite-expanded graphite-epoxy composites electrodes. The zeolite used to prepare the composite electrode was Romanian natural zeolite, which contains about 68 %, wt. clinoptilolite. Each electrode contains 20 %, wt. expanded graphite, and the ratio between expanded graphite and Ag-doped zeolite was 1:1. The electroanalytical performances of both electrodes subjected to the electrode sensitivity, the lowest limit of detection were compared. The Ag-doped zeolite-expanded graphite exhibited the better electroanalytical performance for 4-chlorophenol detection, the lowest limit of detection was 0.002 mM compared with 0.02 mM, which was obtained for expanded graphite-epoxy composite electrode. Taking into account the molecular sieve properties of zeolite, the lowest limit of detection was achieved by applying a chemical preconcentration step prior to the voltammetric determination.

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REFERENCES
1. Mousty C.: Appl. Clay. Sci. *27*, 159 (2004).
2. Carvalho R. H., Lemos F., Lemos M. A. N. D. A, Cabral J. M. S., Ribeiro F. R.: J. Mol. Catal., A *248*, 48 (2006).
3. Carvalho R. H., Lemos M. A. N. D. A, Lemos F., Cabral J. M. S, Ribeiro F. R.: J. Mol. Catal., A *253*, 170 (2006).
4. Granda Valdés M., Pérez-Cordoves A. I., Díaz-Garía M. E.: Trends Anal. Chem. *25*, 1, 24 (2006).
5. Walcarius A., in: *Handbook of Zeolite Science and Technology*, Chap. 14, p. 721, Marcel Dekker, NY 2003.
6. Walcarius A.: Solid. State Electrochem. *10*, 469 (2006).

## PP133

## EVALUATION OF CATALYST ACTIVITY USING REDOX COMPETITION SCANNING ELECTROCHEMICAL MICROSCOPY (RC-SECM)

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Characterisation of catalysts is of fundamental importance for catalyst optimisation and catalyst evaluation with respect to specific conditions in industrial processes. Especially the cathodic oxygen reduction reaction (ORR)[1] in acidic media[2] is of special interest in electrocatalysis due to the complicated 4-electron transfer process. The evaluation of a single catalyst is time consuming and hence the throughput using conventional techniques is limited. Thus, for the evaluation of a large number of catalysts a fast array procedure and an adap -ted investigation method is necessary. In addition to global methods, local investigations are becoming increasingly impor-tant for the evaluation of catalyst properties[3].

For a rapid screening of a multiparameter catalyst system a catalyst library is needed to obtain detailed and comparable information about catalyst properties. Since a large number of industrial catalysts consists of metal nanoclusters deposited on carbon nanoparticles which tend to agglomerate, the materials cannot be dissolved in conventional solvents. Automatic spotting of catalyst suspensions by means of a piezo-actuated microdispenser comply with these requirements. Reproducibility, loading and homogeneity of the deposited catalyst spots can be ensured on a glassy carbon surface. It is possible to produce spots with a diameter of 150 μm in an array in adequate time (Figure 1).

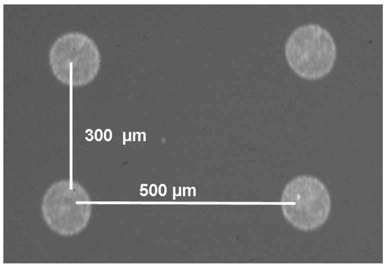

Fig. 1. **Optical micrograph of piezo-dispensed catalyst array**

The local activity of the spots can be visualised with the redox competitions scanning electrochemical microscopy (RC-SECM)[4] with high lateral resolution. An ultramicroelectrode (UME) is positioned next to an active spot using SECM z-approach curves. By applying a potential pulse profile at the SECM tip the catalytic oxygen reduction of the perpendicularly located catalyst spot can be visualized. Essentially, an oxygen decay curve is recorded at each x-, y-position, and the current decrease is modulated by the catalyst's activity.

Local visualisation and determination of catalyst activity was demonstrated using RC-SECM which can bed displayed as image at a certain time or as movie consisting of a sequence of images over the time of the decay curve. By this, a straight forward comparison of different catalyst spots becomes possible. Combinatorial methods for the generation of the catalyst arrays complete the screening procedure. Several factors such as catalyst loading, applied potential at the catalyst modified surface, pH value and temperature are varied to finally elucidate optimal catalyst properties.

Here, formation of catalyst libraries by means of piezo spotting and visualization of local catalyst activity by means of RC-SECM will be presented.

REFERENCES
1. Yeager E.: Electrochim Ac. *29* (11), 1527 (1984).
2. Ziegelbauer J. M., Gullá A. F., O'Laoire C., Urgeghe C., Allen R. J., Mukerjee S.: Electrochim Act. *52*, 6282 (2007).
3. Fernández J. L., White J. M., Sun Y., Tang W., Henkelman G. and Bard A. J.: Langmuir *22*, 10426 (2006).
4. Eckhard K., Chen X., Turcu F. and Schuhmann W.: Phys. Chem. Chem. Phys. *8*, 5359 (2006).

## PP134

## THERMODYNAMICS AND KINETICS OF THE IONS TRANSFER AT THE WATER|NPOE INTERFACE BY MEANS OF THIN FILM SQUARE WAVE VOLTAMMETRY

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Thin-film or three-phase electrodes are assembled of solid electrodes covered with layers or droplets of organic solvents containing redox compounds, in contact with an immiscible aqueous solution. The oxidation or the reduction of the electroactive compound, $M^o$, at the surface of the solid electrode modifies the charge balance in the organic phase; hence the neutrality of the organic phase must be restored by the exchange of an ion with the aqueous medium; oxidation induces ingress of an anion from the water phase or expulsion of a cation from the organic phase. The overall coupled electron-ion transfer reaction is a very convenient system to study charge transfer processes across liquid|liquid interfaces, providing very reliable and accurate results.

Lutetium bisphthalocyanines [$LuPc'_2$] are molecular strongly lipophilic sandwich complexes, which are chemically more stable than ferrocene derivatives that have been frequently used as redox probes to assemble three-phase or thin-film electrodes. Moreover, $LuPc'_2$ can be both reduced and oxidized by reversible one-electron steps. This opens the way to study anion and cation transfers across liquid interface in a single voltammetric experiment. Using this redox probe, Gibbs energies for the transfer across water|nitrobenzene have been measured for a large series of anions and cations[1,2].

The above described methodology was applied to measure both thermodynamic and kinetic parameters of the transfers of a series of anions and cations across nitrophenyloctylether (NPOE)-water interface. The results referring to the energies of ion transfers are compared with literature data[3]. The kinetics of anion transfers was measured by analysing the evolution of the quasireversible maximum of the square-wave voltammetric response[4] and the apparent rate constants have been estimated for the first time.

REFERENCES

1. Quentel F., Mirčeski V., L'Her M. : J. Phys. Chem., B *109*, 1262 (2005).
2. Mirčeski V., Quentel F., L'Her M., Mladenov M., Scholz F., Elleouet C.: J. Phys. Chem., B *109*, 13228 (2005).
3. Wilke S., Zerihun T.: J. Electroanal. Chem. *515*, 52 (2001).
4. Quentel F., Mirčeski V., L'Her M.: Anal. Chem. *77*, 1940 (2005).

## PP135

## GOLD NANOPARTICLES EMBEDDED IN POROUS METAL OXIDE THIN FILMS AS MODIFIERS OF FTO ELECTRODES

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Composite films containing metal nanoparticles have been the focus of many researchers due to their properties for many applications in different fields. In electrochemistry, metal nanoparticles, specially gold nanoparticles, have been found a wide range of electroanalytical and electrocatalytical applications due to their advantages over macroelectrodes. Recently, gold nanoparticles have been used to modified indium tin oxide electrodes to satifactory electrochemical detection of biomolecules such as guanine[1]. In addition to this, gold nanoparticles have been embedded in "sponge-like" silica materials and mesoporous silica films which have demonstrate the advantages of this high surface hibrid materials as precursors of highly active catalysts and as electrochemical sensors[2,3].

In this work, FTO electrodes are modified with high area porous thin films of metal oxides (nanopowder size) containing gold nanoparticules as new electrodes materials. Three different materials ($TiO_2$, MgO and $SnO_2$) have been assayed to include the gold nanoparticles. These new electrode materials have been characterized by means of SEM, TEM, XRD, Surface Plasmon Resonance and Cyclic Voltammetry. Morphology, nanoparticles size distribution and electrochemical behavior of these films have been reported.

REFERENCES

1. Gao Z.: Sens. Actuators, B *123*, 293 (2007).
2. Lin Y., Yantasee W., Fryxell G. E., in: *Dekker Encyclopedia of Nanoscience an Nanotechnology*, p. 1051. Marcel Dekker 2004.
3. Budroni G., Corma A.: Angew. Chem. *45*, 3328 (2006).

## PP136

## ELECTROCHEMICAL ASSESSMENT OF *p*-HYDROXYBENZOATES USING A BORON-DOPED DIAMOND ELECTRODE

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Over the last 80 years, the usage of chemical preservatives in drugs, cosmetics, and food industry has increased. Commonly used synthetic preservatives developed from benzoic acid and hydroxybenzoic acid, such as alkyl para (4)-hydroxybenzoates, so called parabens or alkyl parabens (methyl, ethyl, etc.), act simultaneously as antimicrobial agents and antioxidants and are frequently used as mixed systems. The structural aspects, the lipophilicity parameters, and the different water solubility play concomitantly an important role in a large action spectrum of the products. Various methods for the characterization and analytical evaluation of preservatives have been investigated. However, there are only a few recent studies focussed on the electrochemical study of preservatives from a series of parabens. In this work, the electrochemical behaviour of several parabens preservatives, *i.e.* esters of *p*-hydroxibenzoic acid, methyl-, ethyl- and propyl-4-hydroxy-benzoates (MB, EB, and PB), was investigated at a commercial boron-doped diamond electrode (BDDE), especially in the anodic potential range, in both hydro-alcoholic and aqueous solutions. The electrochemical measurements were carried out in an undivided three-electrode Metrohm cell equipped with a BDDE, a 3mm diameter stationary disc embedded in a Teflon rod as working electrode, a platinum foil counter electrode and a saturated calomel electrode (SCE) as reference. The electrochemical data, *i.e.* cyclic voltammograms (CV) and chronoamperograms (CA) were obtained using an Autolab PGstat 20 Eco Chemie device controlled by a PC running GPES 4.8 version software. Ethanol or methanol, and water were used as solvents for alcoholic and aqueous stock solutions and supporting electrolyte hydro-alcoholic systems, as well. The cyclic voltammetric and chronoamperometric measurements yielded calibration plots with a very good linearity ($R^2$ between 0.975–0.997) and sensitivity, useful for detection and analytical applications. The assessment of the long time stability and the saturation solubility in both double distilled and tap water of the relatively slightly water soluble investigated parabens was easily carried out using electrochemical alternative. Estimated water solubility was correlated with octanol-water partition coefficient.

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## PP137

## POLAROGRAPHIC AND VOLTAMMETRIC BEHAVIOUR OF DESLORATADINE

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Desloratadine (DLOR) is a long-acting non-sedating antihistamine with selective $H_1$-receptor antagonistic activity. Several papers concerning the analytical approach for DLOR determination in plasma are mentioned in literature[1,2]. No literature data dealing with electochemical behaviour or voltammetric methods for DLOR determination were found.

Polarographic behaviour of DLOR was investigated in Britton-Robinson buffer solution of different pH values. Desloratadine exibits single two-electron irreversible reduction wave at pH≥3.5 with half wave potentials shifted from −1.26 V (pH 3.5) to −1.6 V (pH 11). At pH lower than 3.5 the reduction wave overlapped with the hydrogen evolution current that makes the detection impossible. The effect of the pH on the wave current and potential was examined showing the current maximum at pH 9 and the involvement of the $H^+$ ions in the electron transfer process. The nature of this wave was investigated and concluded that the polarographic wave of desloratadine may be atributed to the reduction of the C=N bond of the pyridine ring in the desloratadine molecule. The obtained results are in good agreement with reduction pathway of its parent drug loratadine (LOR) already reported[3]. Other polarographic (dpp) and voltammetric (cv and dpv) techniques were also employed to investigate desloratadine reduction process. The effect of the scan rate on the peak current and potential indicates irreversible, diffusion-controlled process which is strongly influenced by the adsorption of DLOR on the mercury surface. Due to he pronounced adsorption in further work the adsorptive stripping differential pulse voltammograms were recorded with pulse amplitude of 100mV, pulse width of 20 ms, scan speed 20 mV $s^{-1}$, accumulation potential of −1200 mV, accumulation time 30 s. The obtained results showed linear dependence of the peak current with DLOR concentration with good sensitivity and low detection limits.

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REFERENCES

1. Sutherland F. C. W., de Jager A. D., Badenhorst D., Scanes T., Hundt K. H. L., Swart K. J., Hundt A. F.: J. Chromatogr., A *914*, 211 (2001).
2. Yang L., Clement R. P., Kantesaria B., Reyderman L., Beaudry F., Grandmaison C., Donato L., Masse R., Rudewicz P. J.: J. Chromatogr., B *792*, 229 (2003).
3. Ghoneim M. M., Mabrouk M. M., Hassanein A. M., Tawfik A.: J. Pharm. Biomed. Anal. *25*, 933 (2001).

## PP138

## DESLORATADINE DETERMINATION IN REAL URINE SAMPLE USING ADSORPTIVE STRIPPING VOLTAMMETRY

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Desloratadine (DLOR) is a selective peripheral histamine $H_1$-receptor antagonist devoid of any substantial effects on the central and autonomic nervous system[1]. DLOR possesses pharmacological activity similar to its parent drug loratadine (LOR) which undergoes extensive first-pass metabolism in the liver resulting in the DLOR formation. According to pharmacokinetic studies, about 41 % of administered LOR dose is excreted in urine in the form of DLOR[2]. Several reports concerning the analytical approach for LOR and DLOR determination in plasma are mentioned[3,4]. No literature data was found considering voltammetric determination of DLOR neither in spiked nor in real urine sample.

The application of the voltammetric method proposed for DLOR determination in buffer solutions was tested in real human urine. The real urine sample was obtained from the volunteers after the administration of *Pressing*® tablets (Hemofarm concern, SCG). Adsorptive stripping differential pulse voltammograms of DLOR in urine were recorded under the selected conditions. The origin of the peaks was confirmed by standard addition method. The analysis of the voltammograms of the real urine samples led to conclusion that the amounts of DLOR could be traced from sixth hour till the end of the observed period, which is in accordance with literature data[2]. The best chromatographic response of DLOR in real urine was obtained after 12 and 18 hours. Based on these investigations the sensitive AdSDPV method was developed for determination of DLOR in human urine sample. Good selectivity and sensitivity was achieved regarded to the endogenous components of urine matrix, and the obtained results suggested this method for the DLOR monitoring in clinical practice.

*This work was supported by the Ministry for Science of Serbia, Project No. 142071.*

REFERENCES

1. Graul A., Leeson P. A., Castaoer J.: Drugs Future *25*, 339 (2000).
2. Molimard M., Diquet B., Strolin B. M.: Fund. Clin. Pharmacol. *18*, 399 (2004).
3. Yin O. Q. P., Shi X., Chow M. S. S., J. Chromatogr., B *796*, 165 (2003).
4. Liu L., Wang M., Qi P., Li H.: J. Pharm. Biomed. Anal. *34*, 1013 (2004).

## PP139

## THIRD GENERATION BIOSENSOR FOR THE DETERMINATION OF POLYPHENOL INDEX IN FOOD AND BEVERAGES BASED ON NANOBIOCOMPOSITES

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Rigid conducting bionanocomposites represent a simple method for the immobilization of biological and nanostructured materials. These materials showed improved transducing properties for the construction of a wide range of electrochemical biosensors such as immunosensors, genosensors and enzymosensors[1,2].

For the fisrt time, we report direct electron transfer (DET) on graphite-epoxy biocomposites materials based on oxide reductase enzymes. This feature can be also electrochemically demonstrated by the addition of metal nanoparticles made of silver, iron or cupper able to shuttle the catalytic metal site of the enzymes towards the electrochemical transducer in a third generation type of biosensors based on bionanocomposite transducers.

When this material is modified with the enzyme laccase, this material can be used as a third generation biosensor for the determination of total polyphenolic compounds in food and beverages, by applying the potential for the direct oxidation of the enzyme laccase.

The capability of integrating various materials into a single one is their main advantage, besides the improved electrochemical properties compared with other electrochemical devices based on covalent/surface coupling of the enzyme. These materials can be just prepared through ‘dry chemistry’ using procedures that can be easily transferred to mass fabrication of thick film devices. The different properties of these materials are discussed for the first time.

REFERENCES

1. Pividori M. I, Alegret S.: Comp. Anal. Chem. *49*, 439 (2007).
2. Pividori M. I, Alegret S.: Comp. Anal. Chem. *49*, 467 (2007).

## PP140

## ENHANCED ELECTROCHEMICAL PROPERTIES OF MWCNT/POLYSULFONE BASED SCREEN-PRINTED ELECTRODES

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The Polysulfone(PSf)/Multi-walled Carbon Nanotubes (MWCNT) composites were prepared by the phase inversion method as previously reported[1] . Here we describe a profound characterization concerning the composite construction as well as the thermal, electronic, conductive, morphological, physical, chemical and electrochemical properties.

Electrochemical activation of carbon nanotubes was studied in previously[2] , but they presented only electrochemical data and it did not bring any spectroscopic insight why such enhancement happens until Pumera investigations[3]. Moreover, we did not find previous work based on the electrochemical activation of carbon nanotube-based composites. This electrochemical activation was applied (at potentials of

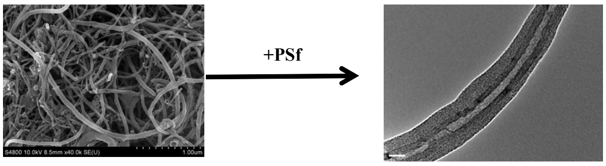

Fig. 1. (left) **SEM image of MWCNT powder and** (right) **TEM of a single MWCNT/ PSf**

1.5–2.0 V *vs*. Ag/AgCl for 60–360 s) to a screen-printed electrode used for cyclic voltammetry of important biomakers such as hydrogen peroxide, ferro/ferricianide, ascorbic acid and dopamine.

The electrochemical activation of MWCNT/PSf composites results in significantly increased electrochemical and catalytic properties. This increase is due to introduction of dramatic wall defects exposing edge planes of MWCNT as well as the diminution of the PSf coating as it was observed by HR-TEM. X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and electrochemical impedance spectroscopy were used to gain deeper understanding the phenomena. XPS revealed a relative increase of presence of carboxyl groups while relative presence of carbonyl and alcohol/ether groups decreases.

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REFERENCES

1. Sanchez S., Pumera M., Fabregas E.: Biosens. Bioelectron. *23*, 332 (2007).
   Sanchez S., Pumera M., Cabruja, E., Fabregas E. : Analyst *132*, 142 (2007).
   Sanchez S., Pérez S., Roldán M., Fàbregas E. : Anal. Chem., accepted.
2. Musameh M., Lawrence N. S., Wang J.: Electrochem. Commun. *7*, 14 (2005).
3. Pumera M. : Langmuir, accepted.

## PP141

## BIOSENSORS BASED ON POLY(VINYLIMIDAZOLE) MICROPARTICLES

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With the aim of solving the problems found in biosensors based on microparticles of polymerized ionic liquid[1], a new polymer microparticles based on a non charged monomer, poly(vinylimidazole) is proposed in this work (Fig. 1).

Biosensors with glucose oxidase (GOx) and polyphenol oxidase (PPO) were designed and applied to determine glucose and polyphenols.

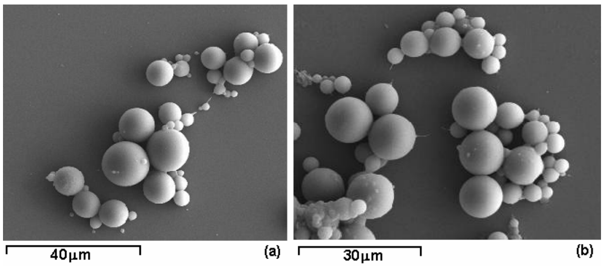

Fig. 1. **SEM micrograph of freeze-dried poly (vinylimidazole) microparticles (a) with GOx** (η=3.2 %) **and (b) PPO** (η=4.0 %)

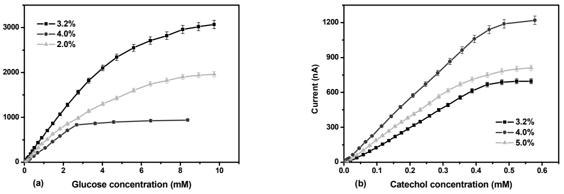

Fig. 2. **Influence of crosslinking on the biosensor response using poly (vinylimidazole) microparticles as immobilization system**. (a) Entrapped GOx: 0.1 M PBS pH 6.0, +0.6 V *vs*. SCE and 25 °C. (b) Entrapped PPO: 0.1 M PBS pH 6.0, −0.1 V *vs*. SCE and 20 °C

In order to optimize the immobilizing system, the effect of the polymer cross-linking ratio for both enzymes and the pH of the synthesis medium have been studied. The influence of analytical parameters such as pH, temperature and enzymatic load have been also investigated. It was established that biosensors based on these polymeric supports can be utilized in aqueous and in non-aqueous medium. Sensitivity, detection limit, linear range and response time of the analytical device were reported for both biosensors in both media.

Glucose was determined in serum samples. To avoid the interference originated by ascorbic and uric acid, a layer of Nafion was included on the electrode surface[1]. A good recovery obtained (98.2–102.1) probe the suitability of the proposed device in this kind of analysis.

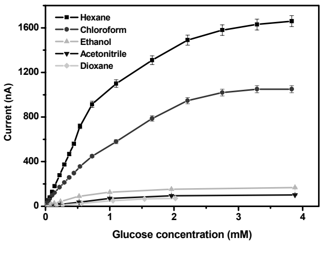

Fig. 3. **Calibration curve of glucose biosensor based on vinylimidazole microparticles**. Experimental conditions: Buffer/organic solvent mixtures (98.5/1.5), +0.6 V and 25 °C

A comparative study of different phenolic compounds was carried with the biosensors based on PPO. The highest affinity of enzyme, and as consequence the response of the biosensor, was found to be for the chlorophenol derivates[2].

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REFERENCES

1. Sánchez-Paniagua López M., Mecerreyes D., López-Cabarcos E., López-Ruiz. B.: Biosens. Bioelectron. *21*, 2320 (2006).
2. Hervas-Perez J. P., Sanchez-Paniagua López M., López Cabarcos E., López-Ruiz B.: Biosens. Bioelectron. *22*, 429 (2006).

## PP142

## DETERMINATION OF ARSENIC(III) USING PLATINUM NANOPARTICLE-MODIFIED SCREEN-PRINTED CARBON-BASED ELECTRODES

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Arsenic is the twentieth most abundant element in the earth's crust. Drinking water rich in arsenic over a long period lead to arsenic poisoning or arsenicosis. Many waters contain some arsenic and excessive concentrations are known to naturally occur in some areas. The health effects are generally delayed and the most effective preventive measure is supply of drinking water low in arsenic concentration. Natural arsenic contamination is a cause for concern in many countries of the world including Argentina, Bangladesh, Chile, China, India, Mexico, Thailand and the United States of America. World Health Organization's (WHO's)[1] Guideline Value for arsenic in drinking water is 10 $\mu$g L$^{-1}$.

Many detection methods have been developed for determination of such levels of arsenic. These include atomic fluorescence spectrometry (AFS)[2], atomic absorption spectrometry (AAS)[3], inductively coupled plasma optical emission spectrometry/mass spectrometry (ICP-OES/MS)[4] and high-performance liquid chromatograph-inductively coupled plasma mass spectrometry (HPLC-ICPMS)[5]. Applying electroanalytical techniques to the determination of trace elements can provide an interesting alternative to the traditional spectroscopic methods. Electrochemical techniques offer two important advantages over the traditional techniques. First of all, the cost of the instrumentation is relatively low and, second, some of these techniques, particularly, stripping voltammetry, are highly sensitive.

Screen-printed electrodes are planar devices with plastic substrates that are coated with layers of electroconductive and insulating inks at a controlled thickness. The advent of screen-printed (thick-film) technology has made it possible to mass-produce inexpensive disposable electrodes for use with electrochemical instruments[6].

The design of new nanoscale materials has acquired ever-greater importance in recent years due to their wideranging applications in various fields. Among these materials, metallic nanoparticles are of great interest due to their important properties and their numerous possible applications. The bibliography lists numerous methods describing the synthesis of metallic nanoparticles in solution as well as by deposition on solid surfaces. Their including chemical synthesis by means of reduction with different reagents, UV light or electron-beam irradiation and electrochemical methods. The latter provides an easy and rapid alternative for the preparation of metallic nanoparticle electrodes in a short space of time.

In this work an environmentally-friendly method for the analysis of As(III) has been developed using carbon screen-printed electrodes (CSPE) modified with platinum nanoparticles.

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REFERENCES

1. *WHO, Arsenic in drinking water*, Geneva, 1993.
2. Ma G., Xie W. B., Liu J., Li X. Y., Jin Y. W.: Spectrosc. Spectr. Anal. *27*, 807 (2007).
3. Niedzielski P.: Anal. Chim. Acta *551*, 199 (2005).
4. Jitmanee K., Oshima M., Motomizu S.: Talanta *66*, 529 (2005).
5. Brennan R. G., Murdock S. A. E. O., Farmand M., Kahen K., Samii S., Gray J. M., Montaser A.: J. Anal. At. Spectrom. *22*, 1199 (2007).
6. Wang J., Lu J., Tian B., Yarnitzky C.: J. Electroanal. Chem. *361*, 77 (1993).

## PP143

## DIRECT ELECTRON TRANSFER OF BOD BOUND AT MWCNT-MODIFIED GOLD ELECTRODES

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Bilirubin oxidase (BOD) is a "blue" multi-copper oxidase, containing 3 different copper centres. The enzyme is able to catalyze the reduction of oxygen to water under physiological conditions at rather high potential. Thus, BOD has found increasingly interest in electrochemical research. In combination with electrodes several mediators have been used. However, also first reports on a direct electrochemical conversion of the enzyme on carbon electrodes have appeared[1–3]. Here we present a study on the electrochemical behaviour of covalently fixed BOD at multi-walled carbon nanotubes (MWCNTs) which are immobilized on gold.

MWCNTs provide a very good environment for protein immobilization and can also effectively replace the natural substrate of BOD – bilirubin. The catalytic reduction current followed linearly the oxygen concentration in solution. The start potential for the catalytic process was 485±10 mV *vs* Ag/AgCl at pH 7. The nanotube modification enabled the bioelectrocatalytic activity of the immobilised BOD; without this modification the enzyme denatured at the gold surface. The stability of the MWCNT-electrode was rather high due to the chemisorption of the nanotubes to gold and covalent linkage of BOD to the nanotubes. With such an electrode system current densities up to 500 μA $cm^{-2}$ are possible (air-saturation). Because of the high activity of the covalently fixed BOD the electrode reaction was limited by substrate diffusion.

In the absence of oxygen the MWCNT-modified surface was also shown to allow a direct voltammetric observation of the conversion of a copper centre of the enzyme. This can be verified by a removal of copper from the protein resulting in a loss of electroactivity. The formal potential was evaluated to be 445±10 mV *vs* Ag/AgCl at pH 7. This is in accordance to recently newly determined values for the T1 copper site[2,4]. It can be also shown that the reduction of this centre is essential for the start of oxygen conversion.

*This work was kindly supported by the Ministerium für Wissenschaft, Forschung und Kultur Brandenburg, Germany (AZ 3508-14-4).*

REFERENCES

1. Shleev S., Kasmi A.E., Ruzgas T., Gorton L.: Electrochem. Commun. *6*, 934 (2004).
2. Tsujimura S., Nakagawa T., Kano K., Ikeda T.: Electrochemistry *72*, 437 (2004).
3. Weigel M., Tritscher E., Lisdat F.: Electrochem. Commun. *9*, 689 (2007).
4. Christenson A., Shleev S., Mano N., Heller A., Gorton L.: Biochim. Biophys. Acta *1757*, 1634 (2006).

## PP144

## NANO ELECTRODES ENSEMBLE (NEE) FOR As (III) DETECTION

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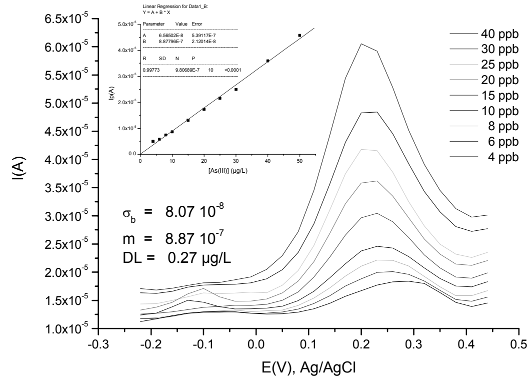
Nanoelectrode ensembles (NEEs) are prepared by electroless template deposition of gold within 80 nm diameter pores of polycarbonate membranes[1]. Taking advantage from the well known improvement in the faradaic to background currents ratio of the nano-electrochemical system[2,3], in the present work the determination of As(III) at NEE was studied by mean of several stripping methods. Characterization experiments as well as the optimization of the analytical procedure are reported. Detection limits of sub μg $l^{-1}$ level are obtained by using the NEEs in combination with square wave anodic stripping voltammetry (SWASV) with a deposition time of 180 s.



A comparison on the analytical performances between ensembles of nanodisk electrodes *vs* ensembles of Au-nanowires[4] is presented and discussed. Surface and morphological information obtained by SEM and AFM are reported.

REFERENCES

1. Pereira F. C., Moretto L. M., De Leo M., Boldrin Zanoni M. V., Ugo P.: Anal. Chim. Acta *575*, 16 (2006).
2. Brunetti B., Ugo P., Moretto L. M., Martin C. R.: J. Electroanal. Chem. *491*, 166 (2000).
3. Menon V. P., Martin C. R.: Anal. Chem. *67*, 1920 (1995).
4. De Leo M., Kuhn A., Ugo P. : Electroanalysis *19*, 227 (2007).

## PP145

## ELECTROCHEMICAL BEHAVIOR OF VERAPAMIL AT A GRAPHITE–POLYURETHANE ELECTRODE

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Recently, graphite composite electrodes using different compositions and agglutinants have been developed as alternative carbon-based electrode materials. This work presents the application of graphite – polyurethane electrodes[1] to study the electrochemical behaviour of verapamil and develop an electroanalytical procedure for its quantification. The influence of pH on the electrochemical behaviour of verapamil was investigated using cyclic voltammetry in different buffer electrolytes in the pH range 1.2 to 11.0, showing a dependence of both peak current and potential on pH. The variation of peak potential with pH of ~60 mV/pH unit suggests a mechanism involving equal numbers of protons and electrons. The best response for the oxidation wave at +0.9 V *vs*. SCE was in 0.2 M acetate buffer at pH 5.3, using a scan rate of 10 mV s$^{-1}$. The results also suggest a diffusion-controlled process, the diffusion coefficient being evaluated as $4.3\times10^{-6}$ cm$^2$ s$^{-1}$.

Electrochemical impedance spectra were recorded at +0.6 V, +0.9 V and +1.0 V (*vs*. SCE), before and after experiments with verapamil in pH 5.3 acetate buffer. No evidence of analyte adsorption was observed.

Square wave voltammetric data showed that the oxidation mechanism involves one electron and proton and best experimental conditions were found to be frequency 25 Hz, amplitude 50 mV and potential increment 10 mV. The detection limit was $8\times10^{-7}$ mol L$^{-1}$, with a linear dynamic range up to $1.3\times10^{-5}$ mol L$^{-1}$. The method was successfully applied to the analysis of the rate of release of verapamil from commercial tablets.

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REFERENCE

1. Mendes R. K., Claro-Neto S., Cavalheiro E. T. G.: Talanta *57*, 909 (2002).

## PP146

## SIGNAL SPLITTING IN THE STRIPPING ANALYSIS OF HEAVY METAL IONS AND METAL-PHTHALATE SYSTEMS USING BISMUTH FILM ELECTRODE

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Since 1922, when Jaroslav Heyrovský described for the first time a certain phenomena from which polarography was gradually developed, mercury has become the most widely used material in working electrodes for electroanalytical purposes. However, its high potential toxicity is an important disadvantage and makes necessary to develop alternative electrode materials, which exhibit an analogous electrochemical behaviour but lower toxicity.

Bismuth film electrode (BiFE) has been proposed as an alternative to the more conventional mercury electrodes, due to bismuth is an environmental friendly element. Some studies developed the application of bismuth film for anodic stripping voltammetry (ASV), a technique that has proved to be useful for the analysis of heavy metal ions due to its excellent detection limits and its sensitivity to the presence of different metal species. Constant-current stripping chronopotentiometry (CCSCP) has been proposed as an alternative to ASV, since it has been empirically proved to be less sensitive to the presence of organic matter, but scarce works have tried to apply bismuth film in this technique.

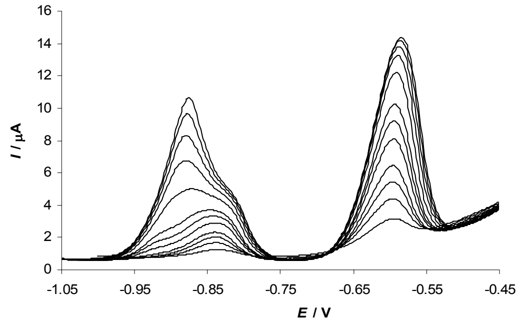

Fig. 1. **Stripping voltammetric determination of Cd(II) and Pb(II) in a BiFE**

The present work tries to complement the findings of these pioneering studies[1,2] with the study of the stripping signals of Pb(II), Cd(II) and Zn(II) by ASV and SCP using a BiFE in a wide range of concentrations (Fig. 1). In the case of Pb(II), regular signals were measured and a good linearity was observed. In contrast, Cd(II) and Zn(II) produced two overlapping signals in both ASV and SCP. One peak is observed at low concentrations of metals and the other one appears when the metal concentration increases. The application of Multivariate Curve Resolution by Alternating Least Squares (MCR-ALS) analysis for the resolution of overlapping peaks shows that in the absence of the second peak, the first signal is linear with the metal concentration and in the presence of both peaks their total area is again linear with the concentration of the metal.

Taking into account these previous results, the influence of deposition parameters in the signal splitting of both Cd(II) and Zn(II) has been studied by ASV and SCP[3], resulting that stripping step is critical in the splitting of Cd(II) signal, while in the case of Zn(II) signal both preconcentration and stripping steps are critical.

In addition, this work tries to test the possibilities of the bismuth–film coated glassy carbon electrode by ASV and SCP for heavy metal speciation. The coexistence of signals at different characteristic potentials anticipates important difficulties in the analysis of potential shifts caused by heavy metal complexation. For analyzing this situation, Pb(II)-phthalate, Cd(II)-phthalate and the Zn(II)-phthalate systems are used as models of small-sized labile complexes in the absence of electrodic adsorption and the results obtained using a BiFE are compared with those obtained using mercury electrodes[4].

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*BQU) and from the Generalitat of Catalonia (project 2005SGR00186).*

REFERENCES

1. Wang J.: Electroanalysis *17*, 1341 (2005).
2. Economou A.: Trends Anal. Chem. *24*, 334 (2005).
3. Serrano N., Alberich A., Díaz-Cruz J. M., Ariño C., Esteban M.: Electrochim. Acta, submitted.
4. Serrano N., Díaz-Cruz J. M., Ariño C., Esteban M.: Electroanalysis *18*, 955 (2006).

## PP147

## CHEMICALLY MODIFIED CARBON PASTE ELECTRODE FOR FAST SCREENING OF OXALIC ACID LEVELS IN SOIL SOLUTIONS

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Soil solution has been described as the aqueous liquid phase of the soil and its solutes, to which plant roots and microorganisms are exposed[1]. Soil solution contains not only species coming from soil, but also from root exudates, by means of which plant reacts. Low molecular weight organic acids e.g. oxalic, malic, citric etc. belong to one group of such exudates, involved mainly in metal complexation and detoxification[2].

In pot experiment, several types of plants were grown on contaminated soil and soil solutions were obtained using nylon suction cup[3]. Analysis of soil solutions by means of voltammetry on HMDE shoved changes in metals complexation with time and therefore fast method for assessing free ligand concentration in soil solution is explored.

Composite electrode, made from carbon powder, lead sulfate and paraffin oil can be used for accumulation of oxalic acid and subsequent oxidation[4]. The voltammetric measurement was performed with medium exchange; oxidation peak at about 1.2 V (Ag/AgCl/$KCl_{sat}$) was measured. With the electrode surface renovation for each curve (employment of teflon holder with movable piston[5]), differential pulse voltammetric measurement can be performed directly in diluted soil solution or after its modification by removing of bound metals on Chelex column. For soil solutions from fluvizem with growing willow, oxalic acid concentrations in range of μM were found. With time for one measurement at about 6 minutes, time changes of soil solution could be followed.

*This work was supported by the grant GAČR No. 521/06/0496.*

REFERENCES

1. Nolan A. L., Lombi E., McLaughlin M. J.: Aust. J. Chem. *56*, 77 (2003).
2. Jones D. L.: Plant Soil *205*, 25 (1998).
3. Jaklová Dytrtová J., Šestáková I., Jakl M., Száková J., Miholová D., Tlustoš P.: Cent. Eur. J. Chem. *6*, 71 (2008).
4. Cai X., Ogorevc B., Tavčar G., Kalcher K.: Electroanalysis 7, 639 (1995).
5. Švancara I., Metelka R., Vytřas K., in: *Sensing in Electroanalysis* (Vytřas K., Kalcher K., ed.), p. 7, Pardubice 2005.

## PP148

## MODIFICATION OF A CARBON PASTE ELECTRODE FOR VOLTAMMETRIC DETERMINATION OF PHENYLHYDRAZINE

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A carbon-paste electrode (CPE) chemically modified with the cobalt(II)-5-nitrosalophen(CoNSaL) as a Schiff base complex was used as a highly sensitive and fairly selective electrochemical sensor for the determination of minor amounts of phenylhydrazine (PHZ). PHZ is a strong oxidant agent, which is extensively used in industry, laboratory and therapeutic setting. A variety of toxic effects of PHZ have been reported, including hemolytic anemia, hypoxia, inflammation, alteration in the liver, kidney, central nervous system, autoimmune disturbance and cancer. The prepared modified electrode shows very efficient electrocatalytic activity for anodic oxidation of PHZ via substantially decreasing of anodic overpotential for PHZ. The mechanism of electrochemical oxidation of PHZ using CoNSal-modified electrode was thoroughly investigated by the cyclic (CV) and differential pulse voltammetry (DPV). The results of the voltammetric studies using the modified electrode show two irreversible anodic waves for the oxidation of PHZ in alkaline pH and only one wave in neutral and acidic media. The obtained linear range for PHZ in DPV measurements was in the range of $10^{-4}$ to $10^{-6}$ M in buffered solution with pH 6.0. The modified electrode has good reproducibility (RSD ≤ 2.5 %), low detection limit ($10^{-7}$ M) and high sensitivity for the detection of PHZ with a very high stability in its voltammetric response. The DPV method using the modified electrode exhibited a reasonable recovery for a relatively wide concentration range of PHZ spiked to synthetic human serum sample.

REFERENCES

1. Shahrokhian S., Fotouhi L.: Sens. Actuators, B *12B*, 942 (2007).
2. Jamasbi E. S., Rouhollahi A., Shahrokhian S., Haghgoo S., Aghajani S.: Electrochim. Talanta *71*, 1669 (2007).
3. Arguello J., Magosso H. A., Landers R., Gushikem Y.: J. Electroanal. Chem. (2008).

## PP149

## MODIFICATION APPLICATION OF CARBON-PASTE ELECTRODE MODIFIED WITH FePc FOR VOLTAMMETRIC DETERMINATON OF EPINEPHRINE IN THE PRESENCE OF ASCORBIC ACID AND URIC ACID

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A carbon-paste electrode (CPE) bulk modified with iron (II)phthalocyanine is used for the sensitive voltammetric determination of epinephrine (EN). The electrochemical response characteristics of EN, ascorbic acid (AA) and uric acid (UA) at the surface of modified electrode is investigated by cyclic and differential pulse voltammetry (CV & DPV). The results show an efficient catalytic activity for the electro-oxidation of EN, which leads to improvement the reversibility and lowering the overpotential more than 100 mV. The effect of pH and potential sweep rate on the mechanism of the electrode process is investigated on the surface of modified electrode. This modified electrode exhibits a potent and persistent electron mediating behavior followed by well-separated oxidation peaks towards EN, AA and UA with good potential differences (AA-EN-UA: 128-345-485 mV). With respect to improved sharpness of the anodic waves on the surface of modified electrode, the resulted peak resolutions are large enough to determine EN in the presence of AA and UA. Under the optimum pH (4.0 by 0.1 M acetate buffer solution), the anodic peak current (in DPV measurements) versus the concentration of EN has a good linear relation in the range of 1 to 300 μM, with the correlation coefficient of 0.998 and the detection limit of 0.5 μM. The prepared modified electrode shows very good accuracy for voltammetric determination of EN in pharmaceutical and clinical preparations and excellent recovery results in spiking to these samples. High sensitivity and selectivity, sub-micromolar detection limit, very good reproducibility together with ease of preparation and regeneration of the electrode surface by simple polishing, make the electrode very suitable for the determination of EN in pharmaceutical and clinical preparations.

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REFERENCES

1. Pihel K., Schroeder T. J., Wightman R. M.: Anal. Chem. *66*, 4532 (1994)
2. Zhang H. M., Wang L. J., Liu Y. Q., Bai C. L.: Electrochim. Acta. *49*, 715 (2004).
3. Shahrokhian S., Ghalkhani M.: Electrochim. Acta. *5*, 2599 (2006).
4. Qiao J. X., Luo H. Q., Li N. B.: Colloids Surf., B. *62*, 31 (2008).

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## PP150

## INVESTIGATION OF THE ELECTROCHEMICAL BEHAVIOR OF CATECHOL AND 4-METHYL CATECHOL IN THE PRESENCE OF METHYL MERCAPTO THIADIAZOLE AS A NOCLEOPHILE: APPLICATION TO ELECTROCHEMICAL SYNTHESIS

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One of the prime principles of green chemistry is to develop an alternative reaction medium, which is the basis for the development of many cleaner chemical technologies and electrochemical synthesis in water. Catechols are a promising group of compounds worthwhile for further investigation, which may lead to the discovery of selective acting, biodegradable agrochemicals having high human, animal and plant compatibility. Preparation and anticonvulsant activity of several derivatives of thiadiazoles have been reported previously. Potential anti-convulsant activities of 1,3,4-thiadiazole derivatives made it a good lead for the synthesis of new compounds. Electro-oxidation of catechol and 4-methyl catechol in the presence of 3-mercapto-5-methyl-1,3,4-thiadiazole as a nucleophile in aqueous buffered solutions was studied by cyclic voltammetry and controlled-potential coulometry. The mechanism of electrochemical reaction is confirmed by spectrophotometric tracing in various times of controlled-potential coulometry. The voltammetric and spectrophotometric foundations indicate that a 1,4 Michael addition of thiadiazole from its thiol moiety to the electrochemically derived *o*-quinone is occurred. The electrochemical synthesis of Michael addition product has been successfully accomplished by controlled-potential coulometry in a divided H-type cell and the reaction product was characterized by spectrophotometric, $^{1}$H and $^{13}$C NMR, elemental analysis and mass spectrometric methods.

REFERENCES

1. Shahrokhian S., Hamzehloei A.: Electrochem. Commun. *5*, 706 (2003).
2. Nekrassova O., Lawrence N. S., Compton R. G.: Electroanalysis *16*, 1285 (2004).
3. Shahrokhian S., Amiri M.: Electrochem. Commun. *7*, 68 (2005).
4. White P. C., Lawrence N. S., Davis J., Campton R. G.: Anal. Chim. Acta *447*, 1 (2001).

## PP151

## MODIFICATION OF GLASSY CARBON ELECTRODE USING NAFION DOPED CARBON NANO PARTICLES: APPLICATION TO VOLTAMMETRIC DETECTION OF GUANINE IN THE PRESENCE OF ADENINE

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Detection of purine bases and purine-containing compounds represent a challenging and important task owing to the importance of these compounds in a variety of biochemical processes. Guanine and adenine are the building blocks of both DNA and RNA that play a crucial role in protein biosynthesis, and the storage of genetic information; in addition, guanine has the lowest oxidation potential and is believed to play a key role in the oxidation of DNA. Recently there have been considerable efforts in the development of electrochemical methods for detection of nucleic acids in biological samples based on guanine oxidation. In this work, a modified glassy carbon electrode using carbon nanoparticles (CNPs) doped with nafion was applied for voltammetric detection of guanine in the presence of adenine. Guanine and adenine produced well-defined oxidation peaks at about +0.6 and +0.9 V, respectively in pH 7 phosphate buffer. Application of the modified electrode resulted in a sensitivity enhancement of about three orders of magnitude in detection of guanine and a negative peak shift up to 0.08 V. The electrode was characterized by using electrochemical methods and atomic force microscopy (AFM). It was found that CNPs enhanced the electroactive surface area and accelerated the rate of electron transfer. Detection limit of guanine was found $1\times10^{-7}$ M (S/N=3) by using differential pulse voltammetry and the linear range in these determinations was from 0.1 to 10 μM. Acid-denatured DNA showed two oxidation peaks corresponding to guanine and adenine residues. The proposed method can be used to estimate the guanine contents in DNA with good selectivity and sensitivity.

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REFERENCES

1. Wang J., Chen G., Muck A., Shin D., Fujishima A.: J. Chromatogr., A *1022*, 207 (2004).
2. Amiri M., Shahrokhian S., Psillakis E., Marken F.: Anal. Chim. Acta *593*, 117 (2007).
3. White B., Smyth R. M., Stuart J. D., Rusling J. F.: J. Am. Chem. Soc. *125*, 6604 (2003).
4. Gao Z.: Sens. Actuators, B *123*, 293 (2007).

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## PP152

## APPLICATION OF CONGO RED SUPPORTED ON MULTI-WALLED CARBON NANOTUBE FOR PREPARATION OF A MODIFIED ELECTRODE IN DETECTION OF URIC ACID IN THE PRESENCE OF GREAT AMOUNT OF ASCORBIC ACID

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Noncovalent immobilization of CR on multi-walled carbon nanotube (MWCNT) (via ultrasonic agitation in aqueous solutions) and its further incorporation within a nafion matrix is described. The prepared composite used for modification of carbon-paste electrode (CPE). The electrochemical response characteristics of uric acid (UA) and ascorbic acid (AA) at the surface of modified electrode is investigated by cyclic and differential pulse voltammetry (CV & DPV). The modified electrode in this work showed an effective and selective electrocatalytic activity for the anodic oxidation of UA and masking the effect of AA and sulfhydryl compounds, which usually considered as interferences in most of the reported modified electrodes. Incorporation of CNT in the matrix of the modified composite enhances the microscopic area and currents in voltammetric investigations. With the noncovalent functionalization by CR, CNTs are efficiently exfoliated into individual nanotubes. In addition, most of the irregular impurities on the sidewall of CNTs are removed, indicating the cleaning role of adsorbed CR. Another interesting feature of CR decorated CNTs is that one of the individual nanotube is bended to nearly a right angle at the middle part and tightly bound with another individual tube at the terminus via sidewall coupling, foreseeing the ability of water-soluble CNTs to form stable and complicated network nanostructures. The effect of pH and potential sweep rate on the mechanism of the electrode process is investigated on the surface of modified electrode. Under the optimum pH (7.0 by 0.1 M phosphate buffer solution), the anodic peak current (in DPV measurements) versus the concentration of UA has a good linear relation in the range of 0.6 to 100 μM, with the correlation coefficient of 0.998 and the detection limit of 0.01 μM. High sensitivity and selectivity and very low detection limit together with the very easy preparation and surface regeneration of the modified electrode and reproducibility of the voltammetric responses makes the prepared modified system very useful in the construction of simple devices for the determination of UA in the presence of large amount of AA in clinical and pharmaceutical preparations.

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REFERENCES

1. Iijima S.: Nature *354*, 56 (1991).
2. Shahrokhian S., Zare-Mehrjardi H. R.: Sens. Actuators,

B *121*, 530 (2007).
3. Ajayan P. M.: Chem. Rev. *99*, 1787 (1999).
4. Sinnott S. B.: J. Nanosci. Nanotech. *2*, 113 (2002).

## PP153
## A STRUCTURAL STUDY OF SURFACE SEGREGATION ON AgCu, AuBi AND AgBi MIXED ELECTRODES

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Increasing focus on environmental surveillance has led to an extensive search for new sensors suitable for electrochemical field analyses. Liquid mercury has in many areas been replaced by solid electrodes which represent an environmental friendly alternative, but solid electrodes in general have a low overpotential towards the hydrogen evolution reaction (HER) in water solutions, and lack the long time stability needed for continuous monitoring.

It has been observed that mixing a compound with low overvoltage towards the HER with only small amounts of a metal having high overvoltage towards HER increases the overall overvoltage towards HER for the mixed metal compound[1]. However, an increase in overvoltage towards HER has also been observed for the alloys of silver and copper, two metals which have quite similar properties concerning the overvoltage towards HER[2]. An additional improved property achieved with mixed electrode materials is increased long time stability[1].

The ionic structures (crystal structure) of various AgCu alloys and AuBi and AgBi mixed metal surfaces will be structurally characterized using surface extended X-ray absorption spectroscopy (SEXAFS). X-ray absorption spectroscopy (XAS) will be preformed to probe long-range structural information of the mixed metals and alloys. From the absorption spectrum, information on structure around absorbing atom on the surface is achieved, and electronic transitions of the surface metals can be obtained from the pre-edge region of the absorption spectrum.

These results will in combination with results obtained from electrochemical characterization by cyclic voltammetry and electrochemical impedance spectroscopy give valuable information about the effect of surface segregation on HER and adsorption processes on alloys and mixed metal surfaces. Results from investigations of the adsorption of hydrogen on various surfaces performed with a scanning electrochemical microscope (SECM) will also be included.

By combining surface characterisation results obtained with the techniques mentioned, a complete picture of the chemistry of the different metals in the alloys is achieved. This information is very important for understanding how the structure of alloys and mixed electrodes influence the kinetics of the hydrogen evolution reaction.

REFERENCES

1. Skogvold S. M.: Electroanalysis *17*, 1938 (2005).
2. Skogvold S. M.: Anal. Bioanal. Chem. *384*, 15673 (2006).

## PP154
## ELECTROCHEMICAL OXIDATION OF BERBERINE

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Berberine is an isoquinoline alkaloid occurring abundantly in plants *Hydrastis canadensis*, *Coptis chinensis* and *Berberis* gen. predominantly in the roots, rhizomes, bark and stems. It is used in traditional Chinese and Indian medicine especially to control blood glucose in diabetes[1], to treat gastroenteritis, diarrhea, to stimulate the immune system and displays anti-tumor, antimicrobial and many others biological and pharmacological activities[2]. Protective effects of berberine against lipoprotein oxidation have been described recently[2,3] showing the antioxidant properties of this compound.

Electrochemical behavior of berberine that can model its biological action has been studied only in reduction mode at a mercury electrode[4]. The goal of the presented work is to report our finding of electro-oxidation of berberine at a glassy carbon and a platinum electrode in nonaqueous and aqueous media in dependence of acidity. Cyclic voltammetry as well as liquid chromatography with amperometric detection were used for this study. The last-mentioned method was optimized for the determination of berberine in plant samples.

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REFERENCES

1. Yin J., Gao Z., Liu D., Liu Z., Ye J.: Am. J. Physiol. Endocrinol. Metab. *294*, E148 (2008).
2. Hung T. M., Lee J. P., Min B. S., Choi J. S., Na M. K., Zhang X. F., Ngoc T. M., Lee I. S., Bae K. H.: Biol. Pharm. Bull. *30*, 1157 (2007).
3. Hsieh Y. S., Kuo W. H., Lin T. W., Chang H. R., Lin T. H., Chen P. N., Chu S. C.: J. Agric. Food Chem. *55*, 10437 (2007).
4. Komorsky-Lovrić Š.: Electroanalysis *12*, 599 (2000).

## PP155

# STRUCTURES OF COBALT AND NICKEL HEXACYANOFERRATE FILMS STUDIED BY EXAFS

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Prussian Blue, the parent species of the numerous family of polynuclear transition hexacyanometallates, is one of the oldest synthetic coordination compounds known. This group of insoluble mixed-valence materials has attracted attention because of the potential application in sensors, batteries, electrochromic devices and optically switchable molecular compounds. There is considerable opportunity for manipulation of material properties by varying either the transition metals forming the network with the alternating cyanide bridges or the univalent alkali metal counter cations occupying interstitial sites. Hexacyanometallates have been studied as powders, pellets, guests in various types of matrices, single crystals or on modified electrodes, and their diversity of stoichiometry and structure are well known due to their high sensitivity to preparative procedures. External control parameters such as illumination, temperature or (as in the present study) applied potential can influence on a range of characteristics, such as electrochromic, thermochromic, ion-exchange, charge storage, mixed valence electrical conductivity, electrocatalytic, optical and magnetic behaviour.

Despite the fact that the quoted applications have generated a wealth of information on metal hexacyanides, structural ambiguities remain. Extended x-ray absorption fine structure (EXAFS) provides valence states, coordination numbers, interatomic distances, root mean square deviation of bond length (i.e. local order or Debye-Waller factor, $2\sigma^2$) and the elemental identities of neighbouring atoms. Since EXAFS can provide such information even for amorphous materials, or materials without long range structural order, it is ideally suited to characterization of electrodeposited thin films on electrode surfaces.

In our study we focus on two representative hexacyanometallates, nickel and cobalt hexacyanoferrate. They were potentiodynamically deposited as thin films on inert electrode surfaces. EXAFS measurements were made in fluorescence mode at Daresbury Laboratory, Warrington, UK, using beamlines 7.1 and 16.5. Measurements were taken at the Fe K-edge (at 7111 eV), the Ni K-edge (at 8333 eV) and the Co K-edge (at 7709 eV) as functions of applied potential. The EXAFS responses, when combined with x-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (IR), yield contrasting patterns of electroactivity and structural change for both materials.

*Acknowledgement: CCLRC Daresbury Laboratory for the EXAFS beam time.*

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## PP156

# VOLTAMMETRIC STUDIES OF 2-GUANIDINOBENZIMIDAZOLE

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2-Guanidinobenzimidazole (2gb, Fig. 1) and some of its derivatives are biologically active compounds. They exhibit physiological activity, an example being the blocking of skin sodium channels. 2gb interacts through the guanidine group with the outward-facing channel entrance forming a labile complex. In addition, 2gb diminishes gastric acid secretion, and also exhibits hypoglycemic and hypotensive properties.

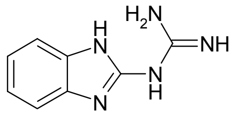

Fig. 1. **2-Guanidinobenzimidazole**

In this study we demonstrate that 2gb catalyzes effectively the hydrogen evolution reaction at a static mercury electrode, which is the basis for its electrochemical characterization and determination. Electrochemical study was carried out by means of cyclic (CV), linear sweep (LSV), differential pulse (DPV), and square wave (SWV) voltammetry. It was observed that the voltammetric response depends on pH of the medium, composition and concentration of buffers, accumulation time and potential, as well as the critical time of the voltammetric experiment. Mechanistic aspects of the electrode reaction have been clarified by CV and SWV, recalling the previous theoretical model[1]. The optimal conditions for analytical determination were obtained in a citrate buffer solution at pH 2.5. The electroanalytical procedure enabled determination of 2gb in the concentration range $6\times10^{-7} - 3\times10^{-6}$ mol L$^{-1}$ by LSV, $4\times10^{-7} - 2\times10^{-6}$ mol L$^{-1}$ by DPV, $1\times10^{-7} - 1\times10^{-6}$ mol L$^{-1}$ by SWV and $8\times10^{-8} - 9\times10^{-7}$ mol L$^{-1}$ by SW preceded by adsorptive accumulation. Repeatability, precision, accuracy of the developed methods just as detection and quantifications limits were determined.

## REFERENCE

1. Mirčeski V., Skrzypek S., Ciesielski W., Sokołowski A. J.: Electroanal. Chem. *585*, 97 (2005).

## PP157

# DETERMINATION OF INORGANIC MERCURY USING A POLYANILINE AND POLYANILINE-METHYLENE BLUE COATED SCREEN-PRINTED CARBON ELECTRODE

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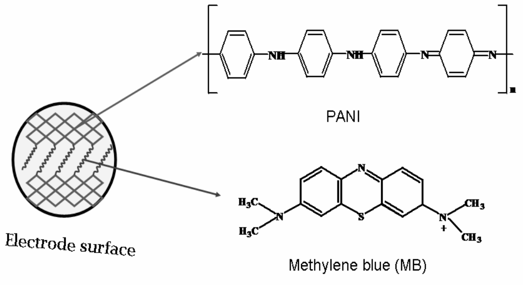
Inorganic mercury ions ($Hg^{2+}$) in laboratory prepared solutions were determined with a screen-printed carbon electrode (SPCE) coated with either polyaniline[1] and polyaniline-methylene blue[2] polymer layers. The electrically-conducting polymers were prepared by chemical polymerisation of monomer solutions of aniline, and mixed solutions of aniline with methylene blue that were drop-coated onto a screen-printed carbon electrode afterwards. Anodic stripping voltammetry (ASV) was used to evaluate a solution composed of [$1\times10^{-6}$ M $HgCl_2$, 0.1 M $H_2SO_4$, 0.5 M HCl], in the presence of the two different polymer combinations. The $Hg^{2+}$ ions were determined as follows, *i*) pre-concentration and reduction on the modified electrode surface, and *ii*) subsequent stripping from the electrode surface during the positive potential sweep. The experimental conditions optimised for $Hg^{2+}$ determination included the supporting electrolyte concentration and the accumulation time[3,4]. The detection limits for the [$1\times10^{-6}$ M $HgCl_2$, 0.1 M $H_2SO_4$, 0.5 M HCl] solution in the presence of the polyaniline and polyaniline-methylene blue modified SPCE were evaluated. The results of the study will be presented to report the use of a conducting polymer modified SPCE as an alternative transducer for the voltammetric stripping and analysis of $Hg^{2+}$ ions.



Scheme 1. **Screen-printed electrode surface coated with polyaniline-methylene blue for anodic stripping voltammetry of inorganic mercury ions**

REFERENCES
1. Somerset V. S., Klink M. J., Sekota M. M. C., Baker P. G. L., Iwuoha E. I.: Anal. Lett. *39*, 1683 (2006).
2. Li X., Zhong M., Sun C., Luo Y.: Mater. Lett. *59*, 3913 (2005).
3. Huang W., Yang C., Zhang S.: Anal. Bioanal. Chem. *374*, 998 (2002).
4. Faller C., Stojko N. Y., Henze G., Brainina K. Z.: Anal. Chim. Acta *396*, 195 (1999).

## PP158

# ELECTROANALYTICAL STUDY OF PHOSPHOLIPID STRUCTURES

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Our attention is devoted to study of behavior of phospholipid structures in aqueous solution. Phospholipids are amphiphilic molecules, analogous to other surfactants, forming in aqueous media different structures depending on their concentration. In higher concentration they form liposomes, polymolecular aggregates organized from closed phospholipid bilayer[1]. These structures of varying size (generally 50 nm to 5 μm in diameter) can encapsulate hydrophobic compound in bilayer membrane or hydrophilic molecules in the internal cavity. Owing to these properties they are used in pharmacology, medical science, molecular biology, food and cosmetic industry for transport of biologically active compounds[2]. Liposomes are more frequently employed in analytical chemistry as (pseudo)stationary phase in the separation techniques[3]. Recently phospholipid vesicles have been prepared by a new method, which is based on spontaneous revesiculation[1]. We study this process of liposomes formation in aqueous phospholipid solution by the different independent electroanalytical methods: electrocapillary and conductivity measurements and linear sweep voltammetry. Last two methods were used for observation of the kinetics of spontaneous revesiculation.

*The financial support of the grant MSM 6198959216 is gratefully acknowledged.*

PREFERENCES
1. Megová M., Műller L., Barták P.: Acta Univ. Palacki. Olomuc., Fac. Rerum Natur., Chemica *47*, 1 (2007).
2. Gregoriadis G. (ed.): *Liposome Technology*. CRP Press, Boca Raton 1984.
3. Burns S. T., Agbodjan A. A., Khaledi M. G.: J. Chromatogr., A *973*, 167 (2002).

## PP159

# GRAPHITE- POLYURETHANE COMPOSITE ELECTRODES FOR STUDIES OF MINOXIDIL

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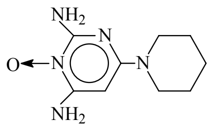
Minoxidil (MX) is a pharmaceutical compound that dilates blood vessels and is used in the treatment of arterial hypertension and in the treatment of *Alopecia Areata*[1].



The purpose of this work was to investigate the voltammetric behavior of MX using a graphite–polyurethane (PU) composite electrode (60 % graphite, w/w), without any surface modification. This new composite[2] has been previously shown to be sensitive and useful in cyclic and square wave voltammetric studies of hydroquinone and atenolol[3,4].

Cyclic voltammetry of MX was performed at the composite electrodes in solutions in the pH range 2.0 to 8.0. The best experimental conditions for electrooxidation of MX were found to be in pH 2.5 Clark and Lubs solutions (HCl/KCl) at scan rate 25 mV $s^{-1}$, the oxidation peak appearing at +0.860 V *vs* SCE. The linear range was from $6.0\times10^{-6}$ to $3.0\times10^{-4}$ mol $L^{-1}$, and the limit of detection was 1.5 μmol $L^{-1}$.

Square wave voltammetry showed a linear range from $2.0\times10^{-6}$ to $1.0\times10^{-3}$ mol $L^{-1}$, and limit of detection 8.0 μmol $L^{-1}$, using optimised experimental conditions of 50 mV amplitude, potential increment 5 mV, and frequency 25 Hz. Square wave voltammograms also demonstrated that the process is irreversible.

Electrochemical impedance spectra were recorded at different applied potentials in blank and in solutions spiked with MX; the results suggested that no adsorption of the MX or its oxidation products occurs on the electrode surface, which permits successive measurements without surface regeneration or renewal, confirming the voltammetric evidence.

*Acknowledgement: CAPES (3176/07-0), CAPES-GRICES (177/07), CNPq, and ICEMS - Coimbra.*

REFERENCES

1. Sousa R. A., Semaan F. S., Baio J. A. F.: Eclética Química *30*, 79 (2005).
2. Mendes R. K., Claro-Neto S., Cavalheiro E. T. G.: Talanta *57*, 909 (2002).
3. Mendes R. K., Cervini P., Cavalheiro E. T. G.: Talanta *68*, 708 (2006).
4. Cervini P., Ramos L. A., Cavalheiro E. T. G.: ACAIJ *2*, 187 (2006).

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## PP160

# NAFION FILM COATED SILVER AMALGAM ELECTRODE FOR DETERMINATION OF TRACE METALS IN PRESENCE OF SURFACE ACTIVE COMPOUNDS

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Anodic stripping voltammetry (ASV) is a highly sensitive and economically reasonable electroanalytical technique for measuring trace metals and one of a few techniques suitable for long time field monitoring of real samples[1].

Direct determination of trace metals in natural samples is often disturbed by presence of surfactants. These substances adsorb at the electrode surface and block it, disturbing deposition of the analyte[2]. Such surface fouling is a limitation in practical ASV application in environmental samples and therefore a big challenge considering use of silver amalgam in long time monitoring stations in the field. The uncoated silver amalgam electrode slowly loses its sensitivity in samples with surface active compounds content during long time use.

This problem can be solved by applying a protective Nafion film layer to decrease adsorption of surface active compounds. Then surfactant species are mechanically blocked from reaching electrode surface, while small metal cations can diffuse through the Nafion membrane.

In this work, performance of silver amalgam electrode was investigated for zinc, cadmium and lead detection in aqueous solutions containing surface active compounds – humic acid and albumin. The performance of uncoated silver amalgam electrode and Nafion coated silver amalgam electrode was compared during repeated stripping experiments. Nafion coating increases sensitivity of the silver amalgam electrode and gives enhanced signal in samples with surface active compounds. The Nafion coating is easy to prepare and the protective effect has a significant value.

REFERENCES

1. Mikkelsen Ø.: Electroanalysis *19*, 2085 (2007).
2. Wang J.: Electroanalysis *13*, 1153 (2001).
3. Kefala G., Economou A., Voulgaropoulos A. : Analyst *129*, 1082 (2004).

## PP161
## LONG TIME MONITORING OF ZINC AND IRON IN WASTE WATER BY USE OF AN AUTOMATIC TRACE METAL SYSTEM

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Monitoring of natural water resources is now at extensive focus[1]. Some recent developments and results in the field of remote monitoring of trace metals in waste water by use of automatic trace metal system (ATMS) are reviewed. This system can be set up to transmit data to computer networks, has a high measuring frequency with possibility for numerous measurements per day, low detection limit and is easy to operate[2]. In this contribution the use of the ATMS for long time monitoring of trace metals is demonstrated. Zinc and iron have been monitored continuously every 30 minutes for a period of 7 months in waste by use of differential pulse anodic stripping voltammetry using solid silver amalgam electrode as a working electrode.

The system shows good calibration curves ($r^2_{avg} = 0.98$) and good stability. Manual maintenance like polishing of the working electrode and cleaning the cell system was carried out once every five days. Additionally, samples were collected manually and analyzed with ICP-MS to get the total concentrations of trace metals.

The possibility to frequently monitor trace metals is a great advantage comparing to random data received from manual sampling and analyses in laboratory. The successful use of solid silver amalgam electrode in waste water for long time monitoring demonstrates the wide range of application and opens new possibilities for environmental surveillance with minimal manual maintenance.

REFERENCES

1. http://ec.europa.eu/environment/water/water-framework/index_en.html
2. Mikkelsen Ø.: Electroanalysis *19*, 2085 (2007).

## PP162
## DETERMINATION OF 5-NITROACENAPHTHENE BY ADSORTIVE VOLTAMMETRY

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In this work we are going to exposed the results obtained of the electrochemical analysis by square wave voltammetry of 5-nitroacenaphthene. This one is a compound belonging to the nitrogenous polycyclical aromatic hydrocarbons, which are derived from the polycyclical aromatic hydrocarbons in this case of the acenaphthene, with two or more aromatic molten rings. These compounds are given as direct or indirect products of the incomplete combustion by means of two different processes: Nitration during the processes of combustion, like in case of the gases of leak of the vehicles diesel, or his formation in the atmosphere from the aromatic polycyclical hydrocarbons.

The aim of this work is the study of 5-nitroacenaphthene due to his incorporation in the lists of carcinogenic substances.

For it an electrochemistry methodology will be design in order to identifier and qualifier the levels of 5-nitroacenaphthene presents in the water of rain. In the first moment the study of the electrochemical behaviour was carried out of 5-nitroacenaphthene by square wave voltammetry in electrode of drop of mercury. The results found on having optimized the physical and chemical variables are that the process is an irreversible reduction, giving a wave of reduction to a potential of −0.4 V. The optimal conditions of the method was used to quantifier and qualifier the presence of 5-nitroacenaphthene in the water of rain.

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## PP163
## DETECTION OF DNA-HYBRIDIZATION WITH Au/Bi ALLOY ELECTRODES

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Beside the usual optical techniques of hybridization detection, electrochemical methods have also been applied increasingly during the last years. The main advantages are that they are inexpensive and easy to use as well as their high efficiency. Usually gold electrodes are used for the detection. There is a lot of scientific research working with other electrode materials, like bismuth[1,2]. Bismuth as electrode material is increasingly used in heavy metal analysis[3] because it is not toxic in contrast to conventionally used mercury, and it offers a high hydrogen overvoltage and adsorption affinity. Unfortunately the disadvantage of the bismuth is the relatively small corrosion resistance. The combination with gold as Au/Bi alloy should improve the corrosion resistance essentially[4].

First investigations with Au/Bi alloy electrodes (96 % Au / 4 % Bi) demonstrated the assumption. After SAM-formation the hybridization with an $[OsO_4(bipy)]$-marked target was carried out. In addition the influence of the target-concentration and the time stability were examined using voltammetric methods.

In summary the results were compared with those at the pure gold electrode.

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REFERENCES

1. Buckova M., Gründler P., Flechsig G.-U.: Electroanalysis *17*, 440 (2005).
2. Adamovski M., Zając A., Gründler P., Flechsig G.-U.: Electrochem. Comm. *8*, 932, (2006).
3. Mikkelsen Ø., Schrøder K. H.: Analyst *125*, 2163, (2000).
4. Duwensee H., Adamovski M., Flechsig G.-U.: Int. J. Electrochem. Sci. *2*, 498 (2007).

## PP164

## NANOSTRUCTURATED CONDUCTING POLYMER BASED BIOSENSORS FOR THE ANALYSIS OF PHENOLIC COMPOUNDS

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Biosensors represent an interesting alternative for the detection of phenolic compounds. Many different approaches can be found in the literature including carbon-nanotube based biosensors[1,2], conducting polymer modified electrodes[3], and silica sol-gel composite films[4]. Some of these methods are relatively complicated, require the use of several reagents and often the biosensor produced presents stability problems. For that reason new alternative biosensor designs for phenolic compounds are needed.

Biosensors based on nanostructured layers[5] have demonstrated to be simple in preparation, allowing the easy electrostatic attractions of biomolecules with minimal protein denaturation during the adsorption process and offering a great promise for developing amperometric biosensors.

Screen-printed carbon electrodes, ITO-coated glass slides and Au electrodes have been modified in this work with polyaniline (PANI) conducting polymer nanolayers and used for the preparation of tyrosinase/laccase-based biosensors.

Optical and electrochemical characterisations have been performed during the preparation of the platforms and showed the efficiency of the Layer-by-Layer (LbL) technique used to modify the electrodes. Some preliminary results related to the detection of phenolic compounds achieved in batch and flow-injection systems and using the different platforms will be also shown.

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REFERENCES

1. Merkoci A., Pumera M., Llopis X., Pérez B., del Valle M., Alegret S.: Trends Anal. Chem. *24*, 9 (2005).
2. Pérez B., Pumera M., del Valle M., Merkoçi A., Alegret S.: J. Nanosci. Nanotech. *5*, 10 (2005).
3. Adeyoju O., Iwuoka E. J., Smyth M. R., Leech D.: Analyst *121*, 1885 (1996).
4. Li J., Chia L. S., Goh N. K., Tan S. N.: Anal. Chim. Acta, 203 (1998).
5. Decher G., Hong J. D.: Macromol. Chem. Macromol. Symp. *46*, 321 (1991).

## PP165

## COPPER DETERMINATION IN ETHANOL FUEL SAMPLES BY ANODIC STRIPPING VOLTAMMETRY AT A GOLD MICROELECTRODE

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A linear sweep anodic stripping voltammetric method was developed for copper determination in commercial ethanol fuel samples by using a gold microelectrode. Under the optimized conditions, it was obtained a linear range from $5.0\times10^{-8}$ to $1.0\times10^{-6}$ mol $L^{-1}$, with detection limit of 22 nmol $L^{-1}$. The developed method was employed to determine copper ions in six commercial ethanol fuel samples and the obtained results were compared with those obtained by FAAS. This study showed that for most of analyzed samples both methods produced concordant results. However, for two samples, cooper is distributed in its labile and complexed forms leading to copper contents contrasting with those obtained by flame atomic absorption spectroscopy (FAAS). It was observed that acidification of the samples is a very efficient way to recover copper from its complexed forms. After acidification, the copper contents obtained were concordant with those obtained by FAAS for all analyzed samples. The results obtained in this work have demonstrated that a gold microelectrode can be successfully employed for copper determination directly in commercial ethanol fuel samples. The proposed method provides some great advances in electroanalysis of copper in this kind of matrix once this is the first work in which both preconcentration and detection step is performed directly in commercial samples without supporting electrolyte addition or pretreatment steps. Thus, the developed method allows copper determination in a fast and simple way with low reagent consumption. Moreover, this work is the first in literature using an electroanalytical technique to provide some insights about the speciation of copper in commercial ethanol fuel samples. The obtained results have shown that acidification of the samples is a very efficient way to recover copper from its complexed forms. In addition, this procedure does not introduce systematic errors in the proposed method.

## PP166

## ANTIMONY- *vs.* BISMUTH-MODIFIED CARBON PASTE ELECTRODES AND RELATED SENSORS IN ELECTROCHEMICAL STRIPPING ANALYSIS

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Antimony and bismuth as the elements of the same group in the periodical system possess similar properties as well as practical usage and e.g. their related behavior in potentiometric pH-measurements is known for more than 80 years[1].

While bismuth-based electrodes are now intensively used in voltammetric measurements as one of the most promising alternative to mercury electrodes[2], related antimony electrodes were of marginal interest until very recently. In contrast to some initial experiments concerning carbon paste electrodes or carbon screen-printed electrodes modified with solid antimony(III) oxide[3,4], newly examined antimony electrodes (namely: antimony film-plated glassy carbon electrode, SbF-GCE[5] and carbon-paste based analogue, SbF-CPE[6]), have been shown to be fairly applicable in more acidic supporting media. In this contribution, some advanced investigations on SbF-CPE, together with initial characterisations of two newest variants, antimony powder-modified carbon paste or carbon ink (Sb-CPE and Sb-SPE, resp.), are discussed in association with possibilities and limitations in electrochemical stripping analysis of heavy metals at the trace concentration level.

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REFERENCES

1. Mehta D. N., Jatkar S. K.: J. Indian Inst. Sci. *18A*, 85 (1935).
2. Svancara I., Vytras K.: Chem. Listy *100*, 90 (2006).
3. Pauliukaite R., Kalcher K., in: *YISAC '01: Young Investigators' Seminar on Analytical Chemistry*, Book of Abstr., pp. 10-11. University of Pardubice, Pardubice 2001.
4. Pauliukaite R., Metelka R., Svancara I., Krolicka A., Bobrowski A., Norkus E., Kalcher K., Vytras K.: Sci. Pap. Univ. Pardubice, Ser. A *10*, 47 (2004).
5. Hocevar S. B., Svancara I., Ogorevc B., Vytras K.: Anal. Chem. *79*, 8639 (2007).
6. Svancara I., Hocevar S. B., Baldrianova L., Tesarova E., Ogorevc B., Vytras K.: Sci. Pap. Univ. Pardubice, Ser. A *13*, 5 (2007).

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## PP167

## ROLE OF HYDROGEN EVOLUTION ON THE REDOX PROCESS OF GUANINE

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More than 25 years it has been known that the nucleobase guanine (G) is reduced on a mercury electrode at negative potentials and its reduction signal is not detectable due to overlapping with the process of hydrogen evolution or the discharge of components of supporting electrolytes[1,2]. Using macroscale controlled potential electrolysis in combination with NMR, the reduction product as 7,8-dihydrogenguanine was confirmed[3]. The microscale electrolysis at mercury electrode recorded by fast scan rates showed that the reduction product can be oxidized back to the original molecule G exhibiting an anodic signal at around –0.2 V *vs.* Ag/AgCl/KCl. The anodic G peak is very analytically useful because the N7 position of G represents the preferred binding sites of antitumour agents, metals or mutagenic substances. The G peak is regarded as an indicator of (a) structure of oligo- and polynucleotide changes, (b) interaction with components in solutions, and (c) different types of covalent adducts[4]. The contribution is aimed at explaining the role of hydrogen reduction (HER) in the redox process of guanine. To elucidate the interrelationship of HER and reduction of guanosine we studied these processes in aqueous solution with tetraethylammonium perchlorate by cyclic voltammetry and elimination voltammetry with linear scan (EVLS)[5] with forward and backward scans. Therefore the negative switching or starting potentials were changed and both reduction processes were evaluated.

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REFERENCES

1. Trnková L., Studničková M., Paleček E.: Bioelectrochem. Bioenerg. *7*, 643 (1980).
2. Paleček E., Jelen F., Trnková L.: Gen. Physiol. Biophys. *5*, 315 (1986).
3. Studničková M., Trnková L., Zetěk J., Glatz Z.: Bioelectrochem. Bioenerg. *21*, 83 (1989).
4. Paleček, E. Jelen, F.: in: *Perspectives in Bioanalysis. Vol. 1. Electrochemistry of nucleic acids and proteins. Towards electrochemical sensors for genomics and proteomics,* Vol. 1 (Paleček E., Scheller F., Wang J., ed.), p. 74. Elsevier, NY 2005.
5. Trnkova L., in: *Utilizing of Bio-Electrochemical and Mathematical Methods in Biological Research* (Adam V., Kizek R., ed.), p. 51. Research Signpost, Kerala 2007.

## PP168

## THE EFFECT OF THICKNESS OF A CAPILLARY WALL ON THE RESPONSE OF CONTACTLESS CONDUCTIVITY DETECTOR

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Capacitively coupled contactless conductivity detectors ($C^4D$) of axial construction have been introduced for applications in capillary electrophoresis in 1998 (ref.[1,2]). The construction comprises two tubular electrodes that are placed around the surface of the silica capillary. Conductivity is measured as the ac-current flowing through the solution phase inside the capillary in response to the high-frequency voltage applied to the two electrodes, which allows suppressing the capacitance component of the total impedance[3]. The distance between the surface of tubular electrode and the inner capillary surface is for the standard fused-silica capillaries typically around 150 μm.

In the present study the effect of thickness of a capillary wall on the response of $C^4D$ is investigated by performing the conductivity measurements in the non-standard capillaries with a much lower wall thickness of ca. 40 μm, which presumable should further suppress the capacitance component. The effect is demonstrated for two background electrolytes, namely, morpholinoethanesulfonic acid (MES)/histidine (His), and the aqueous solution of acetic acid in the broad concentration range.

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REFERENCES

1. Zemann A. J., Schnell E., Volgger D., Bonn G. K.: Anal. Chem. *70*, 563 (1998).
2. da Silva J. A. F., do Lago C. L.: Anal. Chem. *70*, 4339 (1998).
3. Opekar F., Štulík K.: Electroanalysis *18*, 1282 (2006).

## PP169

## AMPEROMETRIC BIOSENSOR BASED ON ACETYLCHOLINESTERASE FOR PARAOXON DETECTION

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As consequence of increasing use of chemicals and biologically active compounds in chemical industry and agriculture, the environmental analytical community continues to search for portable analytical techniques that can give reliable, *on-site* results for a variety of matrices and analytes, as for example pesticides. The toxicity of organophosphorous pesticides is attributed to their ability to inhibit acetylcholinesterase (AChE), which catalyses the hydrolysis of the neurotransmitting agent acetylcholine (ACh). Particularly, the AChE-based biosensors could be used as alarm systems, able to provide an estimation of the global toxicity index of food products or environmental samples[1].

A simple, reproducible and stable AChE amperometric bioelectrode[2–3] was used following two experimental protocols, for measuring the enzyme activity before and after the incubation with paraoxon aqueous solution or dissolved in polar and non-polar solvent. The inhibitory effect of the pesticide induces a decrease of the catalytic activity of AChE. Consequently, less thiocholine (TCh) was produced from ATCh and the current value, due to the TCh oxidation was lower than that recorded in the blank solution and this difference could be correlated with the pesticide concentration.

The aim of this paper was to evaluate the type of inhibition induced by the aquoues paraoxon solution. Also, to demonstrate the influence of polar (acetonitrile) and non-polar (*n*-hexan, *n*-heptan) organic solvents on the activity of the immobilized AChE on a bioelectrode, as well as the synergetic influence of these solvents on the inhibition process induced by paraoxon. A kinetic analysis of the AChE-pesticide interaction process, using Hanes-Woolf linearisation and secondary plots for evaluation of equilibrium dissociation constants, allowed identifying the type of inhibition process. In the same time, the amperometric bioelectrode response allowed evidencing the influence of the organic solvents on the mechanism of AChE inhibition by paraoxon.

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REFERENCES

1. Andreescu S., Barthelmebs L., Marty J.-L.: Anal. Chim. Acta. *464*, 171 (2002).
2. Turdean G. L., in *Recent Trends in Acetylcholinesterase System*, p. 196–245. IOS Press, Netherlands 2005.
3. Turdean G. L., Popescu I. C., Oniciu L., Thevenot D. R.: J. Enzyme Inhib. Medic. Chem. *17*, 107 (2002).

## PP170

## SURFACE GRADIENTS ON BIPOLAR ELECTRODES

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In this contribution, we describe the use of electric fields and imaging optics to produce and analyze surfaces having gradients in chemical properties or molecular functionality. Such surfaces are highly attractive in e.g. sensor and biomi-

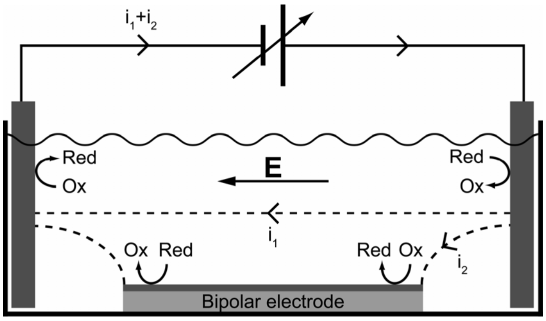

Fig. 1. **Schematic experimental setup, showing the current paths when electrochemical reactions take place on the bipolar electrode**. A variable voltage source is used to control the total current between e.g. two stainless steel electrodes

metic applications. To create a surface gradient, we use a bipolar electrode as a means of establishing a potential gradient across a surface[1]. A voltage (or current) source and two electrodes are used to electrochemically induce an electric field in a solution in which a conducting surface is placed (see Fig. 1). The latter surface can then become a bipolar electrode, i.e. an electrode acting both as an anode and cathode. This occurs when the electric field parallel to the surface exceeds a certain threshold value and thereby induces redox reactions at both ends of the surface. A potential gradient across the electrode is thus induced by the electric field in the solution rather than by controlling the potential of the electrode. Since the potential difference between a point on the bipolar electrode and the solution will vary laterally along the surface, the rates of the reactions will also vary laterally. If the result of such reactions on either end of the bipolar electrode is the adsorption or desorption of a specific molecule, a gradient of that molecule can be created on the surface.

We have used imaging surface plasmon resonance (iSPR) to visualize the electrochemical reactions[2] on a bipolar electrode in real-time. If the refractive index of the solution close to the surface changes when species are being oxidized or reduced, the SPR response will change accordingly. In this way, the potential distribution over the bipolar electrode can also be visualized. We have also used imaging ellipsometry, which via thickness measurements provides a convenient way to evaluate the different steps in the formation of molecular gradients.

Different gradients for various applications can be formed using this method. We have for example prepared gradients of copper as well as of electropolymerized polypyrrole on gold. As a demonstration of the possibility to straightforwardly design and modify surfaces containing chemical property gradients, and the attachment of biorelevant molecules to such surfaces, we have used self-assembled monolayers (SAMs) and protein immobilization procedures. A two-component gradient of thiols was created and lysozyme was coupled to one of the thiols, resulting in a protein gradient. Using imaging ellipsometry, a thickness map of the gradient region was obtained (Fig. 2).

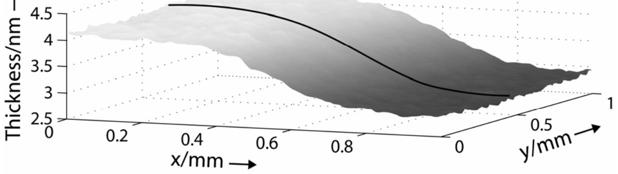

Fig. 2. **Thickness map of the protein gradient with a line in the region from where the line profile was taken**

The present method is a fast and straightforward and does not require access to advanced laboratory equipment. The non-contacted surface can be of virtually any thickness, shape and material. A wide variety of different setup geometries and electrolytes can also be used, making it a very versatile approach. Future studies will include investigations of the composition, degree of phase separation, and organization of thiol gradients using ESCA, scanning probe techniques and, FT-IR microscopy. Different gradient geometries will also be investigated, and details and results from these experiments will be presented.

REFERENCES
1. Ulrich C., Andersson O., Nyholm L., Björefors F.: Angew. Chem. Int. Ed. Engl., in press.
2. Andersson O., Ulrich C., Björefors F., Liedberg B.: submitted.

## PP171
## POROUS MICROELECTRODE ARRAYS FOR NEUROSCIENCE APPLICATIONS

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In order to understand the dynamics of large neural networks, one of the challenges of nowadays neuroscience is to reach the possibility to record large ensembles of neurons simultaneously. In this context, multielectrode arrays (MEA) are gaining a rapidly growing interest. These techniques consist in positioning arrays of microelectrodes in contact with the neural tissue in order to record in parallel a large number of cells. Beside these recording possibilities, MEA also offer the possibility to deliver electrical microstimulations to the neural networks. Another key challenge finally also consists in functionalizing microelectrodes in order to directly detect chemical activity (neurotransmitter release, e.g., glutamate) at the cellular level. However, three major problems become limiting factors when the size of the microelectrodes becomes small :

1) the intrinsic noise level (thermal noise) of the electrode

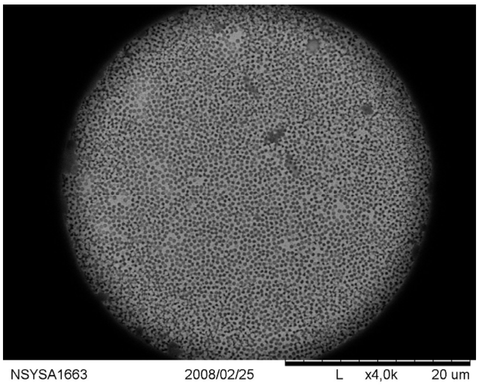

Fig. 1. **SEM image** (top view) **of one porous planar microelectrode** (30 microns diameter) **out of a MEA containing 60 electrodes of this type, used for neurobiological applications**

becomes high which limits the recording sensitivity,

2) the current that can be injected without damaging the electrode material and the neural tissue becomes small and often not sufficient to stimulate the surrounding neurons, and
3) the sensitivity of chemical detection remains poor with a typical microelectrode (~ 100 $\mu m^2$) and much larger electrodes are still required thus preventing detection at the cellular level.

We try to overcome these three limitations by using porous electrodes[1,2], and especially porous microelectrodes recently proposed as analytical tools[3,4]. In order to combine the advantages of an overall small geometric surface with an active surface that is increased by one or two orders of magnitude, standard MEAs are covered with a highly porous metal overlayer. This is achieved by adapting the standard template technique[5] and leads to well defined surfaces as illustrated in Figure 1. These engineered surfaces provide a lower intrinsic noise level for neural network recordings, and increased charge injection efficiency for electrical microstimulation of the central nervous system[6].

REFERENCES

1. Szamocki R., Reculusa S., Ravaine S., Bartlett P. N., Kuhn A., Hempelmann R.: Angew. Chem. Int. Ed. *45*, 1317 (2006).
2. Szamocki R., Velichko A., Mucklich F., Reculusa S., Ravaine S., Neugebauer S., Schuhmann W., Hempelmann R., Kuhn A.: Electrochem. Comm. *9*, 2121 (2007).
3. Evans S. A. G., Elliott J. M., Andrews L. M., Bartlett P. N., Doyle P. J., Denuault G.: Anal. Chem. *74*, 1322 (2002).
4. Szamocki R., Velichko A., Holzapfel C., Mucklich F., Ravaine S., Garrigue P., Sojic N., Hempelmann R., Kuhn A.: Anal. Chem. *79*, 533 (2007).
5. Bartlett P. N., Birkin P. R. , Ghanem M. A.: Chem. Commun. 1671 (2000).
6. Urbanova V., Dubos F., Garrigue P., Yvert B., Vytras K., Kuhn A.: submitted, 2008.

## PP172

## AMPEROMETRIC DETECTION OF NADH WITH CARBON PASTE ELECTRODE INCORPORATING CALCIUM-EXCHANGED ZEOLITE AND METHYLENE BLUE

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Nicotinamide adenine dinucleotide (NADH) is one of the most important coenzymes in the human brain and body. This coenzyme is a common cofactor of about 500 dehydrogenases and its reversible regeneration is a key step in the development of amperometric sensors[1]. The zeolites offer the most complete range of interesting properties required at an electrochemical interface, including shape, size and charge selectivities, physical and chemical stabilities, high ion exchange capacity in a microstructured environment and hydrophilic character. The channels and the cavities of a zeolite framework offer ideal space for incorporation, stabilization and organization of these complex compounds, which often can play the role of redox mediators in different electrode processes[2]. The catalytic nature, activity and other properties of zeolites can be greatly improved by cation-exchange. The versatile cation-exchange behavior of zeolites allows a large number of metal ions and complexes to be incorporated into these materials[3].

In this context, new composite electrode materials consisting of Methylene Blue (as redox mediator), a synthetic zeolite (mesoporous zeolite 13X, Aldrich and a calcium-exchanged zeolite) (as immobilization support) and carbon paste matrix (as conductive material) were designed and tested for NADH amperometric detection. Methylene Blue is a water-soluble cationic dye molecule, suitable to catalyze NADH oxidation[4–6].

The electrochemical properties (formal standard potential, peak currents and peak-to-peak separation) were different in the case of the calcium-exchanged zeolite, probably owing to the formation of a complex between mediator and $Ca^{2+}$. Cyclic voltammetry, rotating disk electrode and amperometry were used to study NADH electrocatalytic oxidation at low overpotentials (0 mV *vs.* $Ag|AgCl/KCl_{sat}$).

REFERENCES

1. Gorton L., Dominguez E., in: *Bioelectrochemistry*, Vol. 9, Electrochemistry of NAD(P)+/NAD(P)H, Encyclopedia of electrochemistry, (Wilson G. S., ed.). Wiley-VCH, Weinheim 2002.
2. Walcarius A.: Anal. Chim. Acta *388*, 79 (1999).
3. Senaratne C., Zhang J., Baker M. D., Bessel C. A., Rolison D. R.: J. Phys. Chem. *100*, 5849 (1996).
4. Gorton L., Dominguez E.: Rev. Mol. Biotechnol. *82*, 371 (2002).
5. Mano N., Kuhn A.: J. Electroanal. Chem. *498*, 58 (2001).
6. Serban S., Murr N. E.: Biosens. Bioelectron. *20*, 161 (2004).

## PP173

## AMPEROMETRIC IMMUNOSENSORS FOR OCHRATOXIN A WITH GOLD NANOPARTICLES ON SCREEN PRINTED ELECTRODES IN STATIC AND FLOW MICROSYSTEMS

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Ochratoxin A (OTA) is a mycotoxin produced by several *Aspergillus* and *Penicilinum* fungi species growing in different agricultural commodities in the field or during feed and food storage. OTA has nephrotoxic, teratogenic, carcinogenic and immunotoxic activity in human and animals. OTA occurs in several foodstuffs such as cereals, coffee beans, nuts and cocoa. There are very strict mycotoxin regulations all over the world[1]. As an instance, the Standing Committee for Foodstuffs recently proposed E.U. regulatory limits for OTA in some agricultural commodities at very low ppb levels.

Official analytical methods available for the analysis of mycotoxins in food and foodstuffs are usually validated on AOAC International Official Methods of Analysis. For OTA, official HPLC methods are available for barley, corn, wheat, coffee, beer, milk, nuts, and wine[2].

Immunochemical methods exhibit high sensitivity and acceptable performance. Many immunological ELISA (enzyme-linked immunosorbent assays) methods are also widely used for *in-situ* and also in screening analysis[3].

The direct voltammetric analysis of OTA is possible[4], because of their electroactivity, but the oxidation of this molecule needs a very high potential (+1.5 V). Besides, sensitivity is low, and then the direct amperometric determination of OTA is not suitable at the level of low-ppb required. For these reasons, using amperometry the use of immobilized antibodies is more convenient.

The aim of the present work is to develop rapid and sensible OTA inmunosensors using advantages of the immunochemical assay and the screen-printed technology.

We used indirect immunoassays in a competitive way by immobilizing OTA-BSA conjugate on the screen-printed carbon electrodes (*SPCEs*) and using AP (or HRP) labelled anti-OTA antibodies. Also we used labelled secondary anti-IgG antibodies to generate the amperometric signal, and poly (vinyl)alcohol or bovine serum albumin (BSA) for blocking and avoid unspecific adsorption.

The electrochemical substrate for generating the amperometric signal was 1-naphtil phosphate (1-NPP). The enzymatic product, 1-naphtol, was detected by differential pulse voltammetry (DPV). The regeneration of the *SPCEs* was also assayed.

We also studied the influence of gold nanoparticles (*AuNPs*, 20 nm diameter) on the amperometric signals of the enzymatically generated 1-naphthol. They were electrochemically deposited from $AuCl_4$- or directly immobilized from stabilized colloidal gold on the working electrode of the *SPCEs*.

Previously to design the amperometric inmunosensors, ELISA checkerboards were assayed for characterizing the OTA-BSA and anti-OTA binding capacities and for optimizing the antibody and antigen dilutions. In these procedures, we used the same OTA-BSA conjugate and labelling with alkaline phosphatase the anti-OTA and anti-IgG, then using 4-nitronaphtyl phosphate as substrate. The enzymatic product 1-nitronaphthol was spectrophotometrically determined at 405 nm.

The use of *AuNPs* on *SPCEs* improved the electrochemical determination of the 1-naphtol. An increased amount of immobilized OTA-BSA conjugate was also observed, and the nanoparticles did not influence the immunoreactions of the OTA with the antibodies

The results obtained with the amperometric inmunosensors were compared with official AOAC methods based on HPLC with fluorescence detection (*t*r: 5.57 min, flow speed: 1.2 $ml\ min^{-1}$, mobile phase: acetonitrile/water/acetic acid; $\lambda_{ecx}$=332 nm, $\lambda_{em}$=457 nm)[3].

This work include the use of a synthesized OTA-*mimic* molecule to be determined with *SPCEs* inmunosensors and their analytical and immunological (ELISA) properties. It is a similar molecule to OTA (we present this molecule to ESEAC-08 in another presentation based on a quartz-crystal microbalance inmunosensor), but it is less toxic and more economic than natural OTA.

In conclusion, *SPCEs* inmunosensors for OTA allow the quick and specific determination of this mycotoxin at the ppb levels. The formation of a layer of nanostructured particles (*AuNPs*) increased the sensitivity of the developed OTA immunosensors.

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REFERENCES

1. Egmond H. P.: Anal. Bioanal. Chem. *389*, 147 (2007).
2. Trucksess M. W.: J. AOAC Int. *89*, 270 (2006).
3. European Mycotoxins Awareness Network: http://www.mycotoxins.org
4. Oliveira S. C. B.: Anal. Chim. Acta *588*, 283 (2007).

## PP174

## ELECTROCHEMICAL QUARTZ-CRYSTAL MICROBALANCE IMMUNOSENSORS FOR NATURAL AND SYNTHETIC OCHRATOXIN A

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Identification and determination of mycotoxins in foods at the nanogram level is nowadays of extremely importance owing to their wide presence and the adverse effects in human

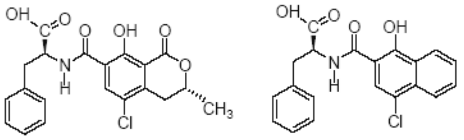

Fig. 1. **a) OTA, b) OTA-mimic**

(and animal) health. There are a great interest in Europe and many other countries in early detection and prevention strategies for decreasing mycotoxin contamination in foods. Legislation in the European Community strictly regulate the maximum contents of mycotoxins (concentration levels from about 0.01 to 10 ppb depending of the kind of food) in foods like cereals, wine, milk, nuts or dried fruit. From all of the wide range of mycotoxins (aflatoxins, deoxyvalenol, zearaleonone, fumonisins…), ochratoxins stands out because of their great toxicity and carcinogenity.

We show the design, optimization and construction of immunosensors[1,2] for Ochratoxin A (OTA), the more toxic ochratoxin, based on an electrochemical quartz-crystal microbalance transducer (*QCM*). The advantage of this technique is the absence of need for labeling (the antigen or antibody) as it is usual in immunoassays, ELISAs (enzyme-linked inmunosorbent analysis) and other kind of immunosensors (e.g. fluorescent or amperometric).

The *QCM* offers the possibility of measuring very small mass changes (~ 18.5 ng/Hz $cm^2$) due to reaction of immobilized OTA conjugate (OTA-BSA) with Anti-OTA in a competitive way. An indirect immunoassay was preferable due to the small molecular weight of the analyte.

The use of biosensors for the *in situ* analytical determination of OTA is evident, but due to the very low levels of OTA in legislative demands, more sensitivity was preferred. Then, we used gold nanoparticles on the Au-quartz surface in order to improve sensitivity of the analytical response.

Gold surface of the quartz crystal was functionalized with a nanostructured self assembled monolayer (SAM), and then gold nanoparticles and the OTA-BSA conjugated were immobilized on the modified metal surface. It was demonstrated that gold nanoparticles (AuNPs, diameter 20 nm) increases the real sensor surface, and then more antigen conjugate (OTA-BSA) molecules were immobilized. Also a greater immunonological binding capacity of the OTA-BSA to anti-OTA antibodies was observed with AuNPs.

We developed a static system arrangement in order to avoid viscosity and density effects (viscoelasticity of the fluids) caused by flowing liquids. We used urea 8 M. for immunosensor regeneration.

On the other hand, a less toxic OTA-*mimic* (see Fig. 1) molecule was chemically synthesized[3] and analytically used onto this *QCM*-inmunosensor. We compare analysis of the natural OTA with the *QCM* transducer nanostructured immunosensor with a validated high-performance liquid chromatography with a molecular fluorescence detector method (*HPLC-FD*).

Moreover, the gold surface roughness[4] was determinated in order to know the real area of the electrode for a reproducible formation of high quality immunosensors. Cyclic voltammetry was used for this purpose. Also we calculated the Sauerbrey's calibration constant of our system (Cf)[5] with three electrochemical methods (Cyclic and differential-pulse voltammetry and chronoamperometry).

Besides, molecularly imprinted polymers (*MIPs*) were made using OTA-*mimic*[3,6], methacrylic acid as functional monomer, 2,2'-azobisisobutyronitrile (*AIBN*) as initiator and ethylene glycol dimethylacrylate (*EGDMA*) as cross linker. These *MIPs* are being used as stationary phase in SPE columns in a flow system connected to a HPLC pump and a fluorescence detector to study elution process and quantification of the OTA. Also, immobilized *MIPs* on gold surface of the *QCM* crystal are being tested as inmunosensors[7]. In this case, the functional monomer of the *MIP* was 4-vinylpyridine, initiator was benzophenone and cross linker was divinylbenzene.

*This work has been financed by the Aragon Government (Science, Technology and University Department) with Project PM 027/2007. Patricia Duato thanks ACP S.A. a research grant.*

REFERENCES

1. Liu M., Li Q. X., Rechnitz G. A.: Anal. Chim. Acta *387*, 29 (1999).
2. Tsai W. C., Hsieh C. K.: Anal. Lett. *40*, 1979 (2007).
3. Baggiani C., Girandi G., Vanni A.: Biosep. *10*, 389 (2002).
4. Hoogvliet J. C., Dijksma M., Kamp B., Van Bennekom W. P.: Anal. Chem. *72*, 2016 (2000).
5. Vatankhah G., Lessard J., Jerkiewicz G., Zolfaghari A., Conway B. E.: Electrochim. Acta *48*, 1613 (2003).
6. Jodlbauer J., Maier N., Lindner W.: J. Chromatogr., A *945*, 45 (2002).
7. Wu A. H., Syu M. J.: Biosens. Bioelectron. *21*, 2345 (2006).

## PP175

## BIOSENSORIC MEASUREMENTS OF L-ASCORBIC ACID AND POLYPHENOLS IN WINE AS FOOD MATRIX

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The characterization of different food samples and food ingredients carries great importance in food quality management as well as in developments of production processes. Because of their structure polyphenols[1] and antioxidants like ascorbic acid[2] are biologically active compounds occuring in many different foods. L-ascorbic acid is widely used as colour stabilizer and natural preservative, since it can highly protect food attributes by preventing oxidation that occurs during

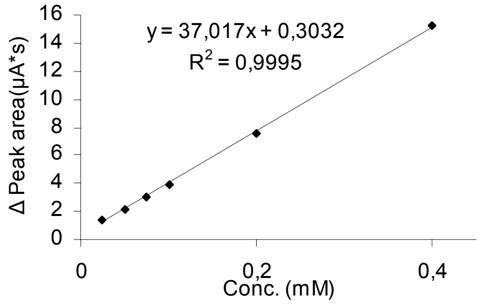

Fig. 1. **Calibration curve of L-ascorbic acid;** (400 mV**,** 100 mM acetate buffer pH 4.7)

processing and storage. Besides polyphenols have an influence on colour, flavour and taste, and they can increase wine quality and hygiene due to their anti-bacterial properties[3]. Different enzyme based biosensors could be used for measurement of these analytes, since they are ideal for quick analysis combined with their resistance for most of interfering components present in general food matrices[4].

In our work enzyme based amperometric biosensors used in flow injection analyzer system were investigated. For detection of analytes ascorbate oxidase and laccase enzyme was immobilized on a natural protein membrane with glutaredialdehyde and fixed into a thin-layer enzyme cell separately from the amperometric detector[5,6]. During the enzymatic reactions the amount of L-ascorbic acid and well defined polyphenols is decreasing, which could be detected at 400mV and 100mV polarizing potential. Using the difference value of enzymatic signal and background signal measured by two sample injectors, one before and one after the enzyme cell, the matrix effect of the real food samples (like in wines) is eliminated.

After optimization of measuring parameters for both systems (flow rate, ionic strength and pH of buffer solution, the working potential, temperature) calibration was carried out with ascorbic acid and catechin standard solutions (fig. 1 and fig. 2). After the statistical evaluation of the measuring system, the spiked ascorbic acid and polyphenol content of wine samples were measured to demonstrate the usability of developed biosensor. The results for content of polyphenols was verified and compared with HPLC method.

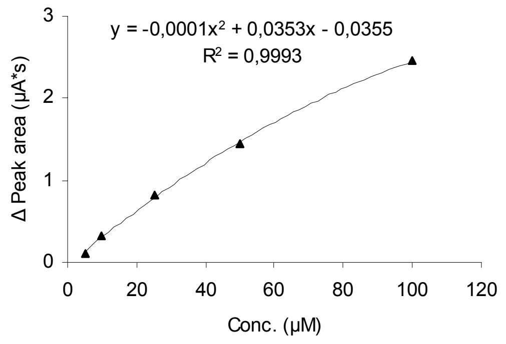

Fig. 2. **Calibration curve of catechin;** (100 mV, 200 mM acetate buffer, pH 5.5)

*Special thanks to all colleagues and EgerFood Regional Research Center application 9/2005 for ensuring research background.*

REFERENCES

1. Nave F., Cabrita M. J., Teixeira da Costa C.: J. Chromatogr., A *1169*, 23 (2007).
2. Clemetson C. A. B.: *Vitamin C*, CRC Press, Boca Raton 1989.
3. Malován S., Montelongo F. I. G., Pérez J. P., Rodríguez-Delgado M. A.: Anal. Chim. Acta *428*, 245 (2001).
4. Kriz K., Anderlund M., Kriz D.: Biosens. Bioelectron. *16*, 363 (2001).
5. Szabó E. E., Adányi N., Váradi M.: Biosens. Bioelectron. *11*, 1051 (1996).
6. Adányi N., Tóth Markus M., Szabó E. E., Váradi M., Sammartino M. P., Tomassetti M., Campanella L.: Anal. Chim. Acta *501*, 219 (2004).

### PP176
### CARBON NANOTUBE FIBER MICROELECTRODES AS SELECTIVE ANALYTICAL TOOLS

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Carbon nanotubes (CNT) have attracted considerable attention in recent years because of their remarkable electronic and mechanical properties[1,2]. Their unique features make them extremely attractive for a wide range of sensing applications especially due to their ability to promote electron – transfer reactions[3–5]. Here, we report on the preparation and interesting electrochemical behaviour of CNT fiber[6] microelectrodes (MFCNT). By combining the advantages of CNTs with those of fiber electrodes, this type of microelectrode[7] differs from CNT modified or CNT containing composite electrodes[8], because it's made exclusively of CNT without any other component like additive or binder. These electrodes have been characterized, among others, with respect to the electrocatalytic oxidation of analytes via deshydrogenase mediated reactions. In this context they have been modified with mediator and their performance could be optimized by increasing the alignment of the nanotubes in the fiber and by increasing the active surface area through a partial exfoliation[9], leading finally to interesting analytical tools[10]. The unmodified CNT fiber electrodes show also a very interesting intrinsic selectivity towards certain analytes of biological or

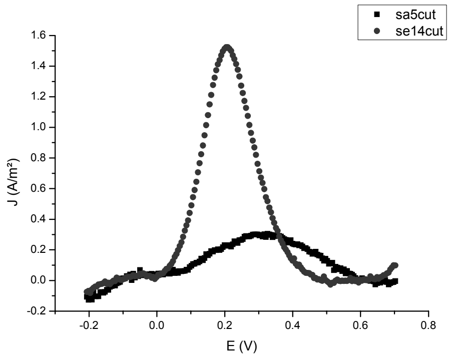

Fig. 1. **Comparison of the reactivity of the CNT fiber electrode with respect to ascorbic acid: stretched fiber with aligned CNTs** (red dotted line), **unstretched fiber with less organized CNTs** (black line)

medical importance. We could for example demonstrate[11] that these new tools are able to discriminate very efficiently ascorbic acid and dopamine, simultaneously present in an electrolyte solution, and this selectivity can be controlled by the alignment of the nanotubes in the fiber electrode (see Fig. 1).

REFERENCES

1. Saito R., Dresselhaus D., Dresselhaus M. S.: Imperial College Press, 1998.
2. Baugman R. H.: Science *297*, 787 (2002).
3. Nugent J. M.: Nano. Lett. *1*, 87 (2001).
4. Sherigara B. S.: Electroanalysis *15*, 9 (2003).
5. Carbon Nanotubes Special issue, Acc. Chem. Res., *35*, 977 (2002).
6. Vigolo B.: Science *290*, 1331 (2000).
7. Wang J.: J. Am. Chem. Soc. *125*, 14706 (2003).
8. Wang J., Musameh M.: Anal. Chem. *75*, 2075 (2003).
9. Viry L.: J. Nanoscience &Nanotechnology *7*, 3373 (2007).
10. Viry L.: Anal. Bioanal. Chem. *389*, 499 (2007).
11. Viry L.: submitted, 2008.

## PP177
## DETERMINATION OF SELENIUM IN RICE SAMPLES BY USING SQUARE WAVE VOLTAMMETRY

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Most of the dietary selenium comes from grain foods such as rice that is a principal food in Thailand. The square wave voltammetric determination of selenium (IV) at a glassy carbon electrode in the presence mercury ions is described. This method was performed in acetate buffer, pH about 4.7 and 0.3 M EDTA. Analytical characteristics of the method proved to be very satisfactory and it is currently being used for foodstuff studies. The concentration of selenium (IV) in acid digestions of rice samples has been determined by using standard addition method and the results were compared with those obtained by a spectroscopic technique. This method can be successfully applied for the determination of selenium in different thai rice samples.

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REFERENCES

1. Recai I., Guler S.: Food Chem. *66*, 381 (1999).
2. David F. L., Nicholas J. T.: Anal. Chim. Acta *408*, 97 (2000).
3. Licheng C., Fangmei Y., Juan X., Yun H., Qiuhui H., Yanling Z., Genxing P.: J. Agric. Food Chem. *50*, 5128 (2002).
4. Franco A. B., Angel A. J. T., Eloy S., Roberto O., Luis D. M. Julio R.: Anal. Chim. Acta *572*, 32 (2006).
5. Monica P., Luigi F., Patrizia M., Giangiacomo B., Roberto M. F.: Food Chem. *105*, 1091 (2007).

## PP178
## VOLTAMMETRIC DETERMINATION OF GENOTOXIC 9-FLUORENONE AT MENISCUS MODIFIED SILVER SOLID AMALGAM ELECTRODE

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The influence of various genotoxic substances on environment and human health is of great importance. The sensitive and selective methods are necessary for the determination of these compounds in complicated matrices. Modern voltammetric techniques can in certain cases fulfill these demands. The studied compound 9-fluorenone (9-FN), known as proven genotoxic agent and structural unit of its carcinogenic nitro derivatives[1], has been determined at meniscus modified silver solid amalgam electrode[2] (m-AgSAE) – a non-toxic alternative to traditional mercury electrodes.

The stock solution was prepared in methanol due to the lower solubility of 9-FN in water. Optimal conditions for 9-FN determination have been investigated in buffered aqueous-methanolic solution. DC voltammetry (DCV) and differential pulse voltammetry (DPV) at m-AgSAE were used. The influence of pH at voltammetric behavior of 9-FN was investigated in methanol – Britton-Robinson buffer solutions (1:1). The concentration dependences were measured under optimum conditions. Limit of determination was around $10^{-6}$ mol $L^{-1}$ for DCV at m-AgSAE and $10^{-7}$ mol $L^{-1}$ for DPV at m-AgSAE. Obtained results have been compared with previous determination of 9-FN at mercury electrodes[3]. An attempt to increase sensitivity using adsorptive stripping voltammetry at m-AgSAE was made. Cyclic voltammetry at m-AgSAE was used to investigate mechanism of reduction of 9-NF at m-AgSAE.

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REFERENCES

1. Sax N. I., Lewis R. J.: *Dangerous Properties of Industrial Materials.* John Wiley & Sons, New York 2000.
2. Barek J., Fischer J., Navratil T., Peckova K., Yosypchuk B.: Sensors *6*, 445 (2006).
3. Vyskocil V., Bologa P., Peckova K., Barek J.: *Proc. 4th International Student Conference* (Opekar F., Svobodova E., ed.), p. 108. Sevcik Consultancy, Prague 2008.

## PP179
## DISSYMETRIC CARBON NANOTUBES BY BIPOLAR ELECTROCHEMISTRY

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We have recently reported an extremely simple « top-down » approach for the generation of carbon nanostructures. After the treatment of a sample of carbon black or HOPG with a polyoxometalate solution stable suspensions of carbon nanoparticles[1] and graphene sheets[2] are obtained respectively. A similar approach can also be used to solubilize carbon nanotubes[3]. These stable suspensions can then be used as a starting point to modify the carbon nanostructures with a metal layer.

Two alternative routes have been used for the metal deposition on these nanoobjects :

a) a simple chemical process based on the metal generation by dismutation[4]. In this case the carbon nanostructures act as nucleation points and a homogeneous metal film is formed.

b) an original process based on bipolar electrochemistry[5], allowing the electrodeposition of metal on the nanostructure without direct contact to an electrode. For that, the stabilized suspension of nanotubes is introduced in a capillary containing an aqueous metal salt solution and a high electric field is applied to orientate and polarize the individual tubes. During their transport through the capillary under sufficient polarization (30 kV) each nanotube is the site of water oxidation on one end, and the site of metal ion reduction on the other end. The size of the formed metal cluster can be controlled and is proportional to the potential drop along the nanotube[6]. This second procedure leads naturally to a highly controlled dissymetric metal deposition as can be seen from the example of selective gold deposition on one end of a nanotube illustrated in Figure 1.

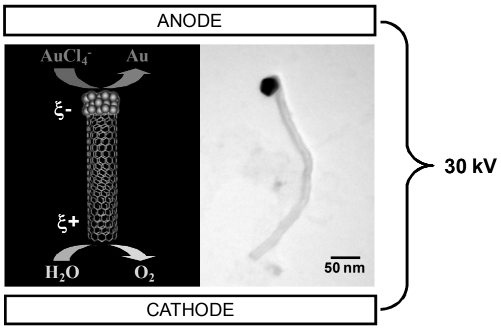

Fig. 1. **Reaction scheme for the site selective generation of a metal cluster** (left); **TEM image of a MWCNT, modified at one end with a gold cluster using the bipolar electrodeposition approach** (right)

This method can be generalized to generate other Janus type nanoobjects and also to form deposits of a very different nature such as other metals, semiconductors or polymers. The approach therefore opens up the way to a whole new family of experiments leading to complex nanoobjects with an increasingly sophisticated design.

The two presented methods are complementary and can be used to tailor nanoobjects with a large variety in shape and morphology, interesting for several applications in the field of nanoscience in general and in particular in analytical chemistry.

REFERENCES

1. Garrigue P., Delville M.-H., Labrugère C., Cloutet E., Kulesza P. J., Morand J. P., Kuhn A.: Chem. Mater. *16*, 2984 (2004).
2. Fattakhova D., Kuhn A.: Carbon *44*, 1942 (2006).
3. Kulesza P. J., Skunik M., Baranowska B., Miecznikowski K., Chojak M., Karnicka K., Frackowiak E., Beguin F., Kuhn A., Delville M.-H., Starobrzynska B., Ernst A.: Electrochim. Acta *51*, 2373 (2006).
4. Li Z., Ravaine V., Ravaine S., Garrigue P., Kuhn A. : Adv. Funct. Mater. *17*, 618 (2007).
5. Bradley J. C., Babu S., Ndungu P.: Fullerenes, Nanotubes and Carbon Nanostructures *13*, 227 (2005).
6. Warakulwit C., Nguyen T., Majimel J., Delville M.-H., Lapeyre V., Garrigue P., Ravaine V., Limtrakul J., Kuhn A. : NanoLett *8*, 500 (2008).

## PP180

# TRACE DETERMINATION OF DNA IN AN AMARYLLIDACEAE PLANT, *Narcissus tazetta* BY SQUARE-WAVE STRIPPING VOLTAMMETRY BASED ON GUANINE SIGNAL

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The bioactive compounds of Amaryllidaceae species, which is one of the largest family of ornamental bulbous plants, are known to possess a wide variety of biological activities including antitumor, antiviral, cytotoxic, anti-inflammatory, antinociceptive, anticholinergic and DNA-binding activities. In view of the potential biopharmacological importance of this family, it is worthwhile to determine the amount of DNA in its species for future studies and potential biotechnological applications perhaps in medicine. The largest genus of Amaryllidaceae, *Narcissus* is naturally grown as well as cultivated in some part of Turkey.

To the best of our knowledge, no literature has been recorded for the determination of DNA in plants by using electrochemical DNA biosensor. In this study, the application of disposable electrochemical DNA biosensor to plant samples is presented.

The DNA biosensor was assembled by immobilizing the double-stranded fish sperm DNA on the surface of a pencil graphite electrode. Square-wave voltammetric scan with the baseline correction was carried out to evaluate the oxidation signal of guanine base. The experimental variables (solution pH, the buffer concentration, immobilization time, stirring speed, square-wave parameters) were carefully investigated. Under the optimal conditions, the increase of the peak was proportional to the DNA concentration in the linear range of 10–50 ng $\mathrm{mL^{-1}}$. The extremely low detection limit (0.36 ng $\mathrm{mL^{-1}}$) was coupled to a good surface-to-surface reproducibility (a relative standard deviation of 7.59 % for five repetitive measurements of 40 ng $\mathrm{mL^{-1}}$). The renewable and low-cost DNA biosensor was successfully applied to the trace determination of DNA isolated from Amaryllidaceae plant, namely *Narcissus tazetta* ssp. *tazetta*.

*This work was supported by the Research Fund of Yuzuncu Yil University, Van, Turkey (Project number: 2007-FED-B44).*

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## PP181

# DIFFERENT PLOTS OF SIGNAL *vs.* TEMPERATURE FOR dsDNA DENATURATION PROCESS IN VOLTAMMETRY AND SPECTROSCOPY

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In this work we report on significant changes that occur in current intensity vs. temperature obtained during dsDNA electrooxidation process. Apparently and thermal denaturation proceed in seen earlier (25–50 °C) in voltammetry compared to the absorbance changes (50–85 °C).

*Calf thymus* double stranded DNA (dsDNA) was investigated in temperature range from 5 to 100 °C. All measurements were done directly without preaccumulation of dsDNA at the lectrode surface and without using any mediator[1]. dsDNA was dissolved in phosphate buffer solution (pH 7.4). Square wave voltammetry, cyclic voltammetry, chronoamperometry and UV spectroscopy were used. In spectroelectrochemical analysis the electrochemical methods were combined with *on line* UV spectroscopy. Glassy carbon- and carbon mesh electrodes were employed in our studies. Specially designed thermal circuit was applied to spectroelectrochemical and spectroscopic measurements.

To monitor the current changes in the dsDNA thermal denaturation process two separated voltammetric signals of guanine and adenine, which correspond to electrochemical oxidation of these bases, were used. It was found that both signals really increase during thermal denaturation of dsDNA, in the range 25 to 50 °C.

In the same temperature region only a small change in absorbance could be seen. Absorbance intensity does change significantly in the adjacent temperature range of 50–85 °C. Spectroelectrochemical measurements showed that even during the electrooxidation process, there was no essential changes in the absorbance in the temperature range 25 to 50 °C. In terms of electrochemichal examination the thermal denaturation process appears to be quite reversible.

Our results do not agree with the results of V. Brabec[2]. He showed that the currents and absorbance intensity obtained during the thermal denaturation process give similar results. However, the electrochemical experiments done by Brabec with dsDNA accumulated at the electrode surface. Dissolved dsDNA might have more possibilities for structural and conformational changes. First, losing the hydrogen bonds and the stacking interactions may be detectable by voltammetry. Second, voltanmetry can be more sensitive to the changes that lead to improved charge transport within dsDNA strand[3].

REFERENCES

1. Nowicka A. M., Zabost E., Donten M., Mazerska Z., Stojek Z.: Bioelectrochem. *70*, 440 (2007).
2. Brabec V.: Biopolymers *18*, 2397 (1979).
3. Giese B., Amaudrut J., Kohler A. K., Spormann M., Wesseley S.: Nature *412*, 318 (2001).

## PP182

## ELECTRODEPOSITION OF THIN LAYERS OF BIRNESSITE: OPTIMIZATION AND APPLICATION

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Birnessite is the major manganese mineral phase in environment[1]. Associated with a very open layered structure, it undergoes cation-exchange reactions and exhibits the largest adsorption capacity on heavy metals than others manganese compounds[2]. Furthermore, Birnessite-type compounds readily participate in oxidation-reduction reactions via a surface mechanism and can react with organic or inorganic compounds[3].

Very few studies report the synthesis of birnessite-type compounds as thin films. However, layers directly deposited on current collectors are attractive and can present potential applications in various fields as hazardous waste remediation or chemical sensors[4] .

That is why, previously[5], we have searched the conditions to electrodeposit thin layers of pure Birnessite onto $SnO_2$, a cheap transparent semiconductor. Now, we optimized the electrodeposition by studying the influence of various parameters as concentration of manganese salt, pH, potential, temperature. In parallel, thin layers were also characterized by XRD and FT-IR for confirming the nature of the compound electrodeposited onto $SnO_2$. From these results, some samples were used for studying interactions as illustration of their potential applications.

REFERENCES

1. Post J. E.: Proc. Natl. Acad. Sci. U.S.A. *96*, 3447 (1999).
2. Feng X. H., Zhai L. M., Tan W. F., Liu, He J. Z.: Environ. Pollut. *147*, 366 (2007).
3. Tebo B. M., Bargar J. R., Clement B. G., Dick G. J., Murray K. J., Parker D., Verity R., Webb S. M.: Annu. Rev. Earth Planet. Sci. *32*, 287 (2004).
4. Suib S. L.: Chem. Innovation *30*, 27 (2000).
5. Larabi-Gruet N., Peulon S., Lacroix A., Chaussé A.: Electrochim. Acta, submitted.

## PP183

## ELECTROANALYSIS OF ADENINE DERIVATES AT GLASSY CARBON ELECTRODE USING FLOW INJECTION ANALYSIS AND LIQUID CHROMATOGRAPHY

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Nucleic acid bases as well as RNA and DNA belong to the most studied molecules. The research of these molecules can be considered as multidisciplinary and, thus, demands cooperation of various branches as analytical chemistry, biochemistry, molecular biology, physics, and others. In the present work we focused on study of basic behaviour of adenine and its derivates (adenosine, *S*-adenosyl-L-methionin, 6-benzyl aminopurine, adenosine monophosphate) in flow system. To measure the target molecules we employed flow injection analysis coupled with electrochemical (CoulochemIII) and UV-VIS detector. Primarily we studied the influence of pHs of Britton Robinson buffer on the responses of adenine and its derivates. The most suitable pH value for determination of the target molecules was 2. Further we measured the dependence of current responses on working electrode potential (hydrodynamic voltammograms). It clearly follows that the optimal working electrode potential was 900 mV. Under the optimized conditions we attempted to determine all target molecules simultaneously. Due to very long time of analysis (more than 40 minutes) we had to mix Britton Robinson buffer with ACN (99:1, %, v/v). We shortened time analysis up to 7 minutes with detection limits below 1 μM.

*We gratefully acknowledge the GA ČR 102/08/1546 for financial support to this work.*

REFERENCES

1. Kizek R., Havran L., Fojta M., Palecek E.: Bioelectrochemistry *55*, 119 (2002).
2. Kizek R., Havran L., Kubicarova T., Yosypchuk B., Heyrovsky M.: Talanta *56*, 915 (2002).
3. Palecek E., Billova S., Havran L., Kizek R., Miculkova A., Jelen F.: Talanta *56*, 919 (2002).
4. Trnkova L., Jelen F., Petrlova J., Adam V., Potesil D., Kizek R.: Sensors *5*, 448 (2005).

## PP184

## HIGH RESOLUTION VOLTAMMETRIC TECHNIQUES: APPLICATION FOR DIRECT SIMULTANEOUS SPECIES DETERMINATION

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The peak overlapping due to the small $E_{1/2}$ difference or

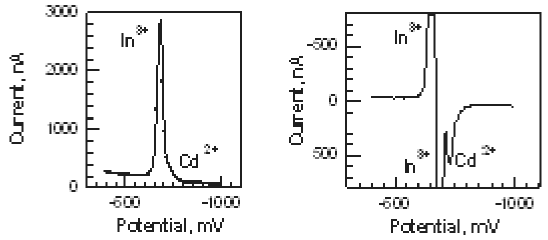

Fig. 1. **DPP** (left) **and DAPV** (right) **voltammograms of In$^{3+}$ and Cd$^{2+}$ at concentration ratio 40:1** ($\Delta E_{1/2}$ = 38 mV)

high concentration ratio or both makes the direct multicomponent trace level voltammetric determinations complicated without preliminary analyte extraction. Employing of some of the second order voltammetric techniques such as RFP[1], DFRP[2], Second Harmonic AC[3] yields distinguished peaks placed on the both side of the zero line even if complete peaks overlapping occurs on the first order voltammetric techniques curves. In spite of their obvious advantages the second order techniques however did not find a wide application because of the complicated equipment needed and problems caused by the high frequency used.

A simple approach applied by the authors recently[4] employing single couples of rectangular alternative polarity pulses combined with an appropriate signal processing yields a true second order voltammetric technique DAPV, providing higher resolution than the conventional first order techniques such as DPP (Fig. 1) and even than the other second order techniques, providing the same sensitivity as DPP.

The applications of this approach to various potential-time waveforms and the comparison of their resolution power and sensitivity is the subject of the present work. Results obtained with couples of species with small $E_{1/2}$ difference such as In(III)/Cd(II) and Pb(II)/Tl(I) at a wide range of concentration ratios will be presented.

REFERENCES

1. Barker G.: Proc. Anal. Div. Chem. Soc. *12*, 179 (1975).
2. Saur D.: Fresenius' J. Anal. Chem. *298*, 128 (1979).
3. Blutstein H., Bond A.: Anal. Chem. *46*, 1531 (1974).
4. Zlatev: J. Electrochem. Comm. *8*, 1699 (2006).

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