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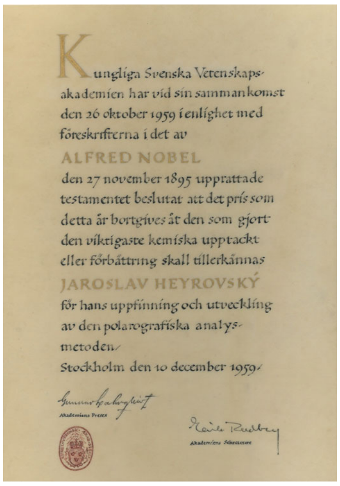
50th Anniversary of Nobel Prize for Polarography

Dear participants of the conference Modern Electroanalytical Methods 2009,

On December 10th, 1959 Professor Jaroslav Heyrovský received from the hands of King of Sweden Gustav Adolph VI Nobel Prize “for his discovery of polarographic method of analysis” as stated on the certificate. To commemorate this event, Czech Chemical Society in cooperation with Faculty of Science of Charles University in Prague and J. Heyrovský Institute of Physical Chemistry of Academy of Sciences of the Czech Republic v.v.i, have decided to organize an international conference Modern Electroanalytical Methods 2009.

Professor Heyrovský receives Nobel Prize for polarographic method of analysis



Kungliga Svenska Vetenskaps-
akademien har vid sin sammankomst
den 26 oktober 1959 i enlighet med
föreskrifterna i det av
ALFRED NOBEL
den 27 november 1895 upprättade
testamentet beslutat att det pris som
detta år bortgives åt den som gjort
den viktigaste kemiska upptäckt
eller förbättring skall tillerkännas
JAROSLAV HEYROVSKÝ
för hans uppfinning och utveckling
av den polarografiska analys-
metoden.
Stockholm den 10 december 1959.

Akademiens Preses

Akademiens Sekreterare

Nobel Prize certificate

Modern electroanalytical methods resulting from the pioneering work of Professor Jaroslav Heyrovský have a significant impact on the practice of many scientific and technological fields, primarily chemistry, biology, medicine, material science and environmental studies and protection. Therefore, the Nobel Prize memorial meeting is dealing with a wide range of contemporary trends in electroanalysis, from important theoretical and methodological developments to the most recent practical applications. There are no invited or keynote lectures, only oral contributions representing the views of individual speakers on the role, possibilities and limitations of modern electroanalytical techniques and their future prospects spanning over the whole wide field of electrochemistry. The state of the art of electroanalytical methods is well documented by quite a number of posters.

We take this opportunity to thank to International Society of Electrochemistry, to Autolab, and IJ Cambria Scientific for kind sponsorship of this event and to all members of scientific and organizing committees for their help.

Have a nice time in Prague

Barek

Jiří Barek
Chairman of the Scientific Committee

Karel Nesměrák

Karel Nesměrák
Chairman of the Organizing Committe

Dear friends,

It is my pleasure to be able to greet you on the occasion of the opening of the meeting. It honors the 50th anniversary of the awarding of the Nobel Prize for chemistry to my esteemed teacher, Prof. Jaroslav Heyrovsky. I had the privilege to work under Prof. Heyrovsky, first for three years at the Charles University in this building, and for sixteen years at the Polarographic Institute of the Czechoslovak Academy of Sciences, where he was the first director since 1950.

I had thus an extensive experience of being in a daily contact with this eminent physical chemist. I was fortunate enough to be able to observe, how well deserved was the Nobel prize awarding to Prof. J. Heyrovsky.

I may point three reasons for which – in my humbly opinion - Prof. Heyrovsky was so successful in not only inventing, but also developing, an important area of electrochemistry. He also formed a school, which supported not only applications of polarography in both practical and theoretical fields, but lead to development of related areas of electrochemistry.

First, Prof. Heyrovsky was able to convey his enthusiasm for research in polarography to his collaborators by showing interest in each of his students at the Charles University by daily inquiring about their results. In the Polarographic Institute he never missed the seminars called “Discussions”. At these seminars, which were held every Thursday, individual co-workers both reported their results and critically evaluated contributions in the journals he selected. Both of the approaches kept him informed about the progress in the applications of polarography.

Second, Prof. Heyrovsky had an outstanding ability to recognize the essential point of a contribution. One of the favorite past-times of the Czechs is mushroom picking. Prof. Heyrovsky was compared to an outstanding mushroom-picker, who would walk on a narrow path, frequented on a given day by numerous searchers, who were not able to find anything, but he would pick up 3 beautiful examples of the Boletus family.

Third, Prof. Heyrovsky was a gentleman, an aristocrat of the spirit, who treated everyone in a most polite manner. But all of the above did not explain the personal magnetism, which influenced everyone he encountered.

I wish his spirit would be manifested in the dealings of this conference. I would also hope that you will have the opportunity, in addition to your work in this building (still alive in my memory), to enjoy the beauty of Prague and its cultural offerings.

Petr Zuman
Honorary President of the Scientific Committee

ORAL PRESENTATIONS

OP-01

NON-TRADITIONAL ELECTRODE MATERIALS FOR ENVIRONMENTAL ELECTROANALYSIS

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The main problem in environmental application of voltammetric and amperometric techniques is the passivation of working electrode. Easy surface renewal of mercury electrodes is not applicable for solid and paste electrodes. However, in many cases problems with passivation can be eliminated by electrochemical treatment of the used electrode, by application of paste electrodes or by the use of electrode materials less prone to passivation. It will be presented on selected examples of environmental applications of solid and paste amalgam electrodes[1], composite electrodes[2] and boron doped diamond film electrodes[3]. Attention will be paid namely to voltammetric and amperometric determination of submicromolar concentrations of environmentally important biologically active organic compounds. Their combination with a preliminary separation and pre-concentration using liquid-liquid or solid phase extraction will be discussed as well.

Financial support from the Ministry of Education, Youth and Sports of the Czech Republic (LC 0603, MSM 0021620857, and RP 14/63).

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OP-02

TRENDS IN ELECTROCHEMICAL TECHNIQUES FOR SURFACE-MODIFIED ELECTROCHEMICAL SENSORS AND BIOSENSORS

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Modern electroanalytical methods have undergone significant progress since the pioneering work of Heyrovsky with dropping mercury electrodes which demonstrated the potentialities of electroanalysis for the first time. Many of the important advantages inherent in the development and use of the dropping mercury electrode have remained of paramount importance, such as electrode surface regeneration and control of adsorption, convection in solution, and applied potential programmes with current sampling which allow lower detection limits and reduce unwanted contributions to the response. The move towards new, solid electrode materials allows a wider potential window to be used for exploiting many oxidation as well as reduction reactions in a variety of solvents. These various advances have led to addressing the challenges of miniaturization[1] and applications in many fields[2,3].

In this paper some of these strategies will be illustrated with respect to recent work carried out with regard to the development of new modified and functionalised solid electrode surfaces for sensors and biosensors, including the use of pulse techniques for increasing sensitivity, use of nanomaterials and nanostructuring the surface. Advances in the use of electrochemical impedance spectroscopy to characterize electrode materials and the electrode-solution interface and application to the development of electrochemical sensors and biosensors will be highlighted. The challenge of analysis in real time will also be addressed.

The continuing support of CEMUC® (Research Unit 285), Portugal is gratefully acknowledged.

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OP-03

ELECTROCHEMICAL ADSORPTION STUDY OF NATURAL ORGANIC MATTER IN MARINE AND FRESHWATER AQUATIC SYSTEMS. A PLEA FOR USE OF MERCURY FOR SCIENTIFIC PURPOSES

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Most biogeochemical processes in natural waters take place at different phase discontinuities, among which the largest one is the atmosphere-ocean boundary. Organic films and surface tension forces provide physical stability of the surface microlayer, where substances, suspended particles and organisms can be concentrated. Owing to molecular properties, surface active chemical species are adsorbed at natural interfaces, *i.e.* their concentration increases spontaneously. The exchange of gases across the sea surface and the fate and effects of airborne contaminant and particulate inputs into the sea are strongly influenced by sea surface microlayer.

Natural films on air-sea boundary, on mineral particles and on the biological interfaces consist of a wide variety of chemical species which have different degrees of surface activity. Measurements of the surface tension of natural films for quantifying surfactants cannot provide satisfactory results. Electrochemical techniques were introduced in measurements of surface active substances in natural waters with much success. The advantage of this approach is the possibility of direct investigation of adsorption characteristics of a complex mixture of naturally present organic solutes at the electrode-electrolyte interface. Among various possibilities of measurement the electrode double layer capacity changes found the widest application. The hydrophobic properties of the mercury electrode surface in sodium chloride solution and /or in seawater can serve as a model that simulates the air-sea phase boundary.

Due to its extreme toxicity mercury is on the list of the priority toxic chemicals and its production, use and distribution will be very limited in near future. In comparison to solid electrodes mercury has many advantages and particularly for adsorption study it is unavoidable because of the smooth, renewable and reproducible surface of the mercury drop, Therefore, the use of mercury with all caution for scientific purposes should be implicit in new environmental regulations.

The financial support of the Croatian Ministry of Science, Education and Sport for the project no. 098-098-2934-2717 under the title “The nature of the organic matter, interaction with microconstituents and surfaces in the environment“ is gratefully acknowledged.

OP-04
GREEN ROUTES FOR CONTROLLED RELEASE GENE FROM MULTILAYER FILMS

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Immobilization of DNA on two dimensional (2D) surfaces and its controlled release without damaging its structure are hot topics of interest in molecular biomedicine and gene therapy in recent years. However, many challenges still exist, due to the lake of materials and approaches to provide spatial and temporal control over the release and delivery of DNA from surfaces.

We present an initial study of tunable DNA release from Zr^{+4}/DNA multilayer films fabricated by LbL assembly. A simple chelation based strategy to trigger DNA released from DNA-incorporated multilayer films is proposed. The films disassembly could be tuned locally by changing chelator and ionic strength. Another strategy to trigger DNA released from Zr^{+4}/DNA multilayer films is to apply an electric field. The disassembly rate of DNA varies with the applied potential leading to controlled release of DNA. Assembly and disassembly of the multilayer films were monitored by SPR, UV-Vis spectroscopy and AFM. We demonstrated the proof of concept of an approach for constructing Zr^{+4}/DNA LbL films capable of selectively releasing precise quantities of DNA on demand in response to small electric potentials. The released pDNA incorporated in the system retains its integrity and transfection activity, and expresses EGFP after being transfected into HEK 293 cells. These green routes studied represent an attractive and efficient gene delivery alternative.

OP-05
SOLID-STATE TRIS(2,2’-BIPYRIDYL) RUTHENIUM ELECTROCHEMILUMINESCENT DETECTOR

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Electrochemiluminescence (ECL) of tris(2,2’-bipyridyl) ruthenium ($Ru(bpy)_3^{2+}$) is usually used as a kind of technique with probe in the solution. Upon the practical and convenient requirement, a solid-state ECL technique has being developed in our laboratory used for common as well as micro-chip detector. By immobilizing $Ru(bpy)_3^{2+}$ on an electrode surface, solid-state ECL provides several advantage over solution-phase ECL, such as reducing consumption of expensive reagent, simplifying experimental design and enhancing the ECL signal and selectivity by functionalized modified electrode. It is developed as useful cost-effective, regenerable solid-state ECL sensors

In this report the state of the art in solid-state $Ru(bpy)_3^{2+}$ mainly based on recent results of our State Key Laboratory of Electroanalytical Chemistry including different fabrications is described. We would stress the use of nanomaterials to increase sensitivity and selectivity, to improve the stability and durability, to make suitability and applicability of this newly developed technique. The solid sensor can also be functionized with cation-exchange polymer like Nafion as well as Eastman AQ at glassy carbon (GC) or carbon nanotube (CNT) as well as silica/AQ/ $Ru(bpy)_3^{2+}$ thin film-modified electrode to increase selectivity significantly. Magnetic nanoparticles and other materials investigated have also investigated to develop cost-effective, regenerable solid-state ECL sensors *etc.* A summary list will be provided in the report. The applications of various solid-state ECL sensors developed in this laboratory for different analytes like amines, oxalates, amino acids, drugs, glucose and biomolecules with low detection limits down to 1 nM even to 1 fM in special case, which will also be provided in the summary list.

Though solid-state ECL sensors with ($Ru(bpy)_3^{2+}$ have been coupled with several techniques *e. g.* capillary electrophoresis, HPLC *etc.* for separation and detection of a wide range of analytes, very few reports have focused on microchip/solid-state ECL. Miniaturized chips exhibit several merits *e. g.* short analysis time, low consumption of reactants and ease of automation, so the combination of the microchip and solid-state ECL sensors using ($Ru(bpy)_3^{2+}$ should have great potential in many analytical applications. We shall deal with this part in our report by our recent results.

This project was supported by the National Natural Science Foundation of China and 863 Project as well as 973 Project.

OP-06
MESOPOROUS (ORGANO)SILICA THIN FILMS FOR ELECTROANALYSIS

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The preparation of silica-based mesoporous thin films via the sol-gel process has been the subject of intense research during the past decade[1]. The most 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. In previous studies, we explored the electrochemical reactivity of these films[2] and evaluated the interest of finely tuned porosity for improving the sensor response towards silver(I) detection[3].

More recently, we developed an original pathway for the deposition of mesoporous (organo)silica thin films[4]. It involves basically the immersion of an electrode in a silica sol containing the hydrolyzed precursors, in the presence of a surfactant template where a cathodic potential is applied to increase the pH locally at the electrode/solution interface and to induce condensation of the precursors. This leads to the formation of well-ordered mesoporous silica films displaying a regular arrangement of mesopore channels oriented normal to the underlying electrode surface (Fig. 1). These films have been characterized by various physico-chemical techniques (cyclic voltammetry, crystal quartz microbalance, scanning and transmission electron microscopies, X-ray diffraction). A special attention was given to highlight the effect of electro-deposition conditions and sol compositions on the film properties[5], and also on the electroanalytical performance of the modified electrode for copper(II) detection[6].

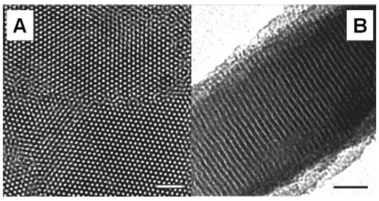

Fig. 1. **SEM picture of electrodeposited mesoporous silica thin film.** Scale bar is 20 nm

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OP-07
MERCURY ELECTRODES AS UNIQUE TOOLS FOR NUCLEIC ACIDS STUDIES

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The beginnings of nucleic acids (NA) electrochemistry were connected with application of polarographic techniques inherently employing the dropping mercury electrode. Oscillopolarographic, and later differential pulse and alternating current polarographic studies of DNA brought fundamental discoveries not only in the field of bioelectrochemistry, but also in the area of nucleic acids structure and dynamics (such a polymorphy of the DNA double helix or DNA premelting). Later, the hanging mercury drop electrode (HMDE) and adsorptive stripping voltammetric methods were introduced which made it possible to increase considerably the sensitivity of DNA determination, as well as to develop novel analytical approaches based on DNA-modified electrodes.

Although nowadays the main interest of electrochemists and other scientist involved in the development of electrochemical DNA sensors is focused on application of non--mercury (carbon, gold, other metallic or semiconductor) electrodes, often modified with self-assembled monolayers, conductive polymers or other interfaces, various mercury-based electrodes (including HMDE, mercury film or solid amalgam electrodes) remain unique tools for nucleic acids analysis. In contrast to the perhaps most popular carbon electrodes, the mercury and some amalgam ones allow highly structure-sensitive measurements of DNA without any DNA labeling. Thus, subtle changes in the double-stranded DNA structure, including those induced by DNA superhelicity, binding of intercalative drugs or formation of strand breaks can easily be monitored. In addition, electrode processes involving catalytic hydrogen evolution at the mercury electrodes have been utilized to determine with a high sensitivity DNA labeled with osmium or platinum complexes. Recent data suggest that catalytic processes yielded at the mercury by unlabeled proteins can be utilized for monitoring DNA-protein interactions.

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OP-08
INTERMETALLIC COMPOUNDS Cu_xZn STUDIED WITH AGNES

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AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) is a new electroanalytical technique specifically developed to measure the free metal concentration of amalgamating elements[1]. The novelty of the technique is that, by the end of the preconcentration stage, Nernstian equilibrium for the analyte is attained. The technique has successfully determined Zn, Cd and Pb in synthetic and real samples (such as seawater[2] and wine[3]). Given that there is no commercial Ion Selective Electrode for the determination of free Zn in solution, AGNES could become a relevant method for this purpose. Recently, anomalous stripping current for high Zn concentrations (relative to the background electrolyte concentration) have been discussed[4]. The existence of intermetallic compounds of Cu^0 and Zn^0 in the amalgam is well described in the literature[5] and can lead to an interference in the standard application of AGNES to determine free Zn(II) when Cu (II) is present.

A large number of experiments where AGNES has been applied to mixtures of Zn(II) and Cu(II) can be rationalized with a simple theory based on 2 hypotheses: *i)* The intermetallic compounds are not reoxidized in the standard AGNES stripping stage, and *ii)* Equilibrium conditions for the intermetallic compounds are reached within the (relatively long) deposition times. The interpretation of the results is helped by the consideration of 2 diagrams of the phases (*i.e.,* precipitated Cu^0, Zn^0 or several intermetallic compounds Cu_xZn) expected in the amalgam under given conditions.

The knowledge of the conditions for the appearance of the intermetallic compounds leads to the suggestion and evaluation of strategies to avoid such interference in the application of AGNES to determine free Zn concentration.

This work was supported by the Spanish Ministry of Education and Science (Projects CTQ2006-14385 and CTM2006-13583), by the "Comissionat per a Universitats i Recerca del Departament d'Innovació, Universitats i Empresa de la Generalitat de Catalunya" and by the European Social Fund.

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OP-09
SPECIATION OF Fe(III) AND V(V) IN SUPPORTED CATALYSTS BY VOLTAMMETRY OF MICROPARTICLES

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In the last decade, voltammetry of microparticles (VMP) has successfully been applied to the analysis of solids. It has also contributed to several solid-state speciation studies, a particular branch of analysis, not accessed by majority of methods traditionally perceived as "chemical analytical". The direct identification of individual forms of analyzed ions in solid specimens is urgently asked for by materials chemistry, a branch of chemistry exceeding the traditional "textbook" divisions of chemistry. The development of analytical sciences must follow the developments in the synthesis laboratories not to endanger its future, and the chemical materials belong to a niche rather sparsely occupied by the contemporary analytical chemistry. The "materials characterization and testing" is mostly focused on physical properties of specimens, and so solid-state speciation by chemical analytical means is yet not satisfied practical requirement. And VMP is an option here.

Fe(III) modified alumosilicates belong to arsenal of chemical materials of the last two decades. The individual forms of Fe(III) ions in supports, namely zeolite framework species, superficial free ionic species, their oligomers, and superficial nano- and microcrystalline oxide particles, exhibit quite different catalytic performance. The solid-state speciation of Fe(III) is currently mainly performed by diffuse reflectance UV-Vis spectroscopy, and VMP has been very helpful here[2,3].

The relationships between individual species and their performance are also very specific for supported V(V) catalysts. The identification of the supported V(V) species has been hindered by their nature in the non-traditional "grey zone" between free ionic and particulate oxide forms. Raman and UV-Vis spectroscopies, thermally programmed reduction, and also VMP (ref.[4]) have contributed to their description.

Voltammetric analysis of catalysts has been funded by projects 104/07/1400 (GACR) and AV0Z40320502 (MŠMT).

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OP-10

ABSOLUTE POTENTIALS OF STANDARD REFERENCE ELECTRODES AT 25 °C

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Recently[1], standard potentials (E^o, NHE = 0) in aqueous solutions were found to be linearly dependent on the ionization potentials (I) with a common intercept at $I = 0$ of 4.20 ± 0.03V for all redox couples except for halogens, which was 2.87 ± 0.01V. These two values are the absolute potentials of NHE for the H^+/H and $1/2H_2/H^-$ equilibria respectively. The former value is exactly the same as that obtained experimentally and is close to that suggested earlier. This has now enabled obtaining the absolute potentials (E^o_{abs}) of the reference electrodes, which were hitherto referred to that of NHE (arbitrarily as zero). The results are assembled in Tab. I.

Table I
Absolute potentials of reference electrodes at 25 °C (ref.[2])

Electrode	E^o [V]	E^o_{abs} [V]
Hydrogen electrode (NHE)	0.00	4.20
Calomel electrode		
• Hg/Hg_2Cl_2, KCl (1M) – NCE	0.28	4.48
• Hg/Hg_2Cl_2, KCl (saturated) – SCE	0.24	4.44
Silver / silver chloride		
• Ag/AgCl, KCl (0.1M)	0.29	4.49
• Ag/AgCl, KCl (saturated)	0.20	4.40
• Ag/AgCl, NaCl (saturated)	0.20	4.40
Mercury / mercury oxide:		
• Hg/HgO, NaOH (0.1M)	0.17	4.37
Mercury / mercurous sulfate		
• Hg/Hg_2SO_4, H_2SO_4 (1M)	0.67	4.87
• Hg/Hg_2SO_4, K_2SO_4 (saturated)	0.65	4.85
Silver / silver sulfate		
• Ag/Ag_2SO_4, H_2SO_4 (1M)	0.71	4.91
• Ag/Ag_2SO_4, K_2SO_4 (saturated)	0.69	4.89

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OP-11

VOLTAMMETRIC BEHAVIOUR OF ALUMINIUM POWDER IN AQUEOUS DISPERSION

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Aluminium powder prepared by "electric explosion of wires" (ref.[1]) at the Tomsk Polytechnic University was dispersed in water and the deaerated dispersion was electrolysed by linear cyclic voltammetry with hanging mercury drop electrode.

The powder particles are accumulations of spheres of diameters 30–200 nm. Due to storage open to air and moisture the metallic core of the spheres is covered by an inner layer of aluminium oxide, then aluminium oxo-hydroxide, and the outer layer consists of $Al(OH)_3$ (ref.[2]).

Although aluminium hydroxy compounds are "insoluble" in water, after 3 min of activation by ultra-sound the dispersion in pure water yields voltammograms showing electroactivity of hydrolytic products of aluminium particles consisting in charging current and in evolution of hydrogen[3].

The charging current produces a prominent peak in the middle of the potential span of the anodic branch of the cyclic voltammogram due to change in adsorption of positively charged intermediate hydrolytic aggregates of aluminium hydroxide[4]. Value of pH of the aqueous dispersion spontaneously increases and when it exceeds 8, the charging current peak disappears.

At higher concentration of powder particles the cathodic current of hydrogen evolution shows irregular flashes due to partial particular mechanism of electrode process[2].

With rate of anodic scan of 500 mV/sec on the curve appears anodic oxidation of aluminium amalgam. The amalgam is formed electrochemically from aluminium hydrolytic products at sufficiently negative potentials together with hydrogen, and from direct interactions of bared particle metallic cores with mercury.

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OP-12
EXTENDED VIOLOGENS – THEIR ELECTROCHEMICAL AND ADSORPTION PROPERTIES ON MERCURY

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Extended viologens represent a group of the organic molecules that are intended to be used as molecular wires in the molecular electronic devices[1,2]. Molecular wires refer to conducting objects that are of a molecular scale diameter with the length exceeding to microscopic dimensions. The follow-up chemical processes should not complicate the electron transfer steps in such systems. In this contribution the electrochemical and adsorption properties of a series of organic molecules consisting of the repeated extended viologen units of the type shown below were studied on the mercury electrode using cyclic voltammetry, DC polarography and AC voltammetry.

Even in the organic solvents the reduc-tion is accompanied by the adsorption of these molecules on the electrode surface. In a water/ethanol mixture all compounds form a compact film in a wide potential range close to the potential of zero charge. At more negative potentials the molecules undergo the reduction in their adsorbed form. Time-resolved differential capacity measurements showed that the differential capacity reaches a constant value of 2.3 μF cm^{-2} independent of the temperature, the length and the bulk concentration of the wire. In the micromolar concentration range time needed to fully cover the electrode surface is independent of the electrode potential and the adsorption is controlled by the diffusion process. The surface concentration can be calculated using the Koryta equation and for the wire with $n = 1$ this value is 5.2×10^{-11} mol cm^{-2}, which gives the area per molecule equal to approximately 320 Å. Based on the space-filling model and the constant differential capacity value in the compact film region we can conclude that the extended viologen molecules lie flat on the mercury electrode surface.

Financial support from GA AV (IAA400400802), Grant Agency of the Czech Republic (GACR 203/08/1157) and Ministry of Education (LC510, COST OC140) is greatly acknowledged.

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OP-13
10th DECEMBER 1959: JAROSLAV HEYROVSKÝ AND NOBEL PRIZE

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Shortly, the way of Jaroslav Heyrovský to the Nobel Prize in chemistry is described. In detail, the occurrences of the day December 10th, 1959 – when Heyrovský took over the Nobel Prize from the hands of the Swedish king Gustav Adolf VI – are presented.

OP-14
SOME MEDITATION ON POLAROGRAPHY

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I spent nearly all my professional life with polarography and about twenty years under the leadership and management of professor Heyrovský. At the jubilee of awarding the Nobel prize to J. Heyrovský I should like commemorate in few words the direct important contribution of the Heyrovsky polarography to electroanalytical chemistry as well as some electrochemical methods, originated apparently only intuitively from polarography (including methods for quality assessment, *e. g.* the voltammetric tongue).

OP-15
LIQUID|LIQUID INTERFACE IN ELECTROCHEMICAL DETECTION OF BIOMOLECULES

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Electrochemical detection of biomolecules at metal|solution interface is hardly possible. The non-electroactive ions cause only a minor effect on electrochemistry of the interface: even double layer capacitance is independent of their concentration. Second, the dimensions of biomolecules are much larger, than the dimensions of the double layer.

After pioneer publication of Koryta electrochemistry of interface between two immiscible liquids became an important tool of electroanalytical chemistry. Ions, which are redox inactive at metal solution interface become electroactive at liquid|liquid interface. Classic four-electrode setup, however, was poorly applicable for detection of biomolecules. Alternatively, a thin layer of organic liquid, containing a dissolved electroactive solute, is placed on a working electrode surface and submerged in an aqueous electrolyte solution with common reference and counter electrodes. Oxidation of electroactive material within the organic phase has to be associated with the counterion transfer from water, so as to keep the electrical neutrality within the organic phase.

Thermodynamics of ion transfer across the liquid|liquid interface at a solid electrode shielded with a thin layer of water-immiscible organic solvent has been investigated. We have found that for less polar organic solvents the formal potential is mainly determined by the enthalpy of the anion transfer across the liquid|liquid interface, whereas the entropy term of the Gibbs free energy causes only a minor effect.

We observed voltammetric response to protein transfer from water to reversed micelles in organic solvent. Varying proteins and surfactants, as well as polarity of organic solvent, we proved that the observed raise in current of shielded electrodes, which in certain cases exceeds background by the two orders of magnitude, is indeed provided by the presence of proteins. Sensitivity of the system is dependent on protein dimensions as well as on its interfacial properties.

Analytical applications of the electrochemical observation of protein transfer across liquid|liquid interface are possible due to dependence of the peak current on protein concentration. Selectivity of the system can be addressed by the selectivity of protein extraction into organic phase.

A novel electrochemical approach for label-free detection of DNA primary sequence has been proposed. The reported sensor was suitable for discrimination of a single mismatch oligonucleotide from the full complementary one.

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OP-16
UNUSUAL MICROELECTRODES FOR BIOANALYSIS

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Microelectrodes have become an essential tool in modern electroanalysis with a wide range of applications especially in the field of biology and medicine. In this context we've developed and studied recently somewhat unusual microelectrodes that can be fine-tuned in terms of their physico-chemical properties either by giving them an internal porosity[1–3] or by using carbon nanotubes for their elaboration[4,5], with the ultimate "microelectrode" being actually a single nanotube addressable by an external field[6]. In this presentation we will describe the elaboration of such electrodes, their properties as well as their potential applications in different areas of analytical chemistry.

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OP-17
DETECTION OF *IN VITRO* DAMAGE TO DNA USING CARBON ELECTRODES IN FLOW-THROUGH CELL

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The main types of DNA damage include interruptions of the sugar-phosphate backbone (strand breaks), release of bases due to hydrolysis of *N*-glycosidic bonds and a variety of nucleobase lesions. Among others, electrochemical techniques were proven as highly sensitive tools for the DNA damage detection[1]. Electrochemical biosensors have been used not only to detect, but also to induce and control DNA damage at the electrode surface via electrochemical generation of the damaging (usually radical) species[2,3]. Label-free detection of strand breaks with mercury-based DNA sensors and measurements of intrinsic DNA signals due to the guanine residue belong to the most frequently applied techniques. The $[Co(phen)_3]^{3+}$ redox indicator-based detection was described to test DNA degradation and antioxidative substances preserving DNA from its damage[1].

Here, a disposable DNA biosensor created calf thymus dsDNA layer deposited on screen-printed carbon electrode and arranged in a commercial electrochemical flow-through cell. The biosensor is applied to the evaluation of DNA damage by the Fenton reaction agents by using cyclic voltammetry peak current and peak to peak potential separation of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox indicator in solution. Electro-chemical impedance spectroscopy is used for the verification of changes at the DNA layer[4]. Antioxidative effects of standard chemicals and plant extracts are also detected.

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OP-18
HISTORY OF ELECTROANALYTICAL METHODS

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Though there are many historical reviews on electrochemistry as well as on analytical chemistry, hardly any compact overview on the history of electroanalytical methods exists. This contribution is an approach to provide a rather compact chronology of electroanalysis. An assay is made to give a short overview on the development of different electroanalytical methods (for both direct determinations and indication in volumetry), electrodes and electrochemical sensors.

Electrogravimetry belongs to the oldest quantitative procedures introduced 1864 by Wolcott Gibbs[1]. Roots are even older and are represented by "voltameters". Closely related to electrogravimetry is coulometry which is also based on Faraday's laws. Early applications comprise determinations of atomic masses (19th century) and coulometric determination of thin metal layers at the beginning of the 20th century.

Conductivity measurements are also a rather old analytical method which was applied (with direct current) in 1829 already. The effective procedure was developed in the 1860s after the use of alternating current by Kohlrausch[2]. Nernst equation[3] (1889) was the base for direct potentiometry, *e. g.*, determination of sparingly soluble electrolytes. Max Cremer[4] is accredited as the inventor of the glass electrode (1906), which is the first electrochemical sensor. Potentiometric indication of titrations by Robert Behrend[5] (1883) was the first instrumental indication in volumetric analysis.

The invention of polarography by Jaroslav Heyrovský[6] (1922) is the starting point of wide application of electroanalysis with the dropping mercury electrode. The polarograph, developed in cooperation with Masuro Shikata[7], was the first automated analytical device in history. As a follow-up various methods (pulse methods, alternating current and others) as well as voltammetry including stripping analysis have gained increasing importance.

Further development of electroanalysis is characterized by new electrodes and electrode materials, *e. g.*, stationary mercury electrodes, carbon-paste electrodes, chemically modified electrodes, and increased application of electrochemical sensors, *e. g.*, heterogeneous carbon sensors[8].

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OP-19
USE OF LFER FOR INVESTIGATIONS OF INTRAMOLECULAR INTERACTIONS IN FISCHER AMINOCARBENE COMPLEXES

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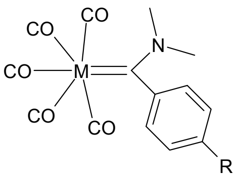
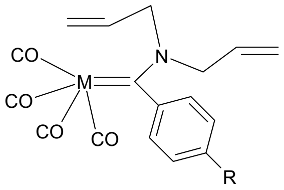
The presented contribution should illustrate the significance of classical electrochemical approach for experimental investigation of intramolecular electronic interactions and displacement of HOMO and LUMO orbitals in new coordination compounds – promising catalysts and synthetic building blocks. The detailed interpretation of the acquired data correlated with theoretical calculations leads to understanding of the relationship between structure and redox or spectroscopic properties of studied compounds. This knowledge is a basis for targeted design of next generation of compounds and enables prediction of their behaviour.





Several series of Fischer-type M(0) – aminocarbene complexes (M = Cr[1], W, Fe) with or without chelating allylic ligand and with various substituents R (*see* Figure) were investigated polarographically at a DME and voltammetrically at a Pt-electrode in strictly aprotic dimethylformamide. The use of the LFER (Linear Free Energy Relationship) treatment based on the correlation of reduction or oxidation potentials with corresponding Hammett sigma substituent constants helped substantially to the elucidation of the differences in reduction mechanisms, to the localization of oxidation and reduction centers in the molecule, to the evaluation of the role of sterical hindrance and to the explanation of differences between Cr and Fe complexes as well as between the chelated and non-chelated compounds.

Electrochemical results were supported by NMR measurements and by calculation of optimized structures, MO energies and vibrational analyses using Gaussian 03 program package and hybrid B3LYP functional.

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OP-20

FLOW INJECTION DIFFERENTIAL PULSE – ANODIC STRIPPING VOLTAMMETRY AS A TOOL FOR THALLIUM MONITORING IN THE ENVIRONMENT

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Thallium is an element which is highly toxic for humans, animals, micro-organisms and plants. The toxic effect of the element is closely related to its mobility. Fortunately, the major part of thallium in soil is usually strongly entrapped in the parent matter and is practically immovable. Even *aqua regia* extraction does not significantly mobilize entrapped thallium[1]. However, this is not the case with pyrites and lead-zinc ores, the processing of which is the main source of thallium pollution. Therefore, surface water, bottom sediments and soil from areas where these ores are mined and processed should be monitored[2,3]. Mobility of thallium in soil can be determined by sequential extraction.

Monitoring thallium in the water and water soluble fraction of soil requires adequate analytical tools. Extremely low thallium concentrations should be determined. Flow injection differential pulse – anodic stripping voltammetry (FI-DP--ASV) is a competitive leader among analytical methods. Thallium concentration below 1 pM was determined in real environmental samples[4]. In the case of poor background, due to a dissolved matrix, medium exchange ensures precise thallium determination.

Thallium in fractions of soil derived from divergent geological backgrounds, in stream and rivulet water, as well as in bottom sediments was monitored using FI-DP-ASV.

This work was supported by the Ministry of Science and Higher Education (grant 0841/B/PO1/2008/35).

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OP-21

SIMULTANEOUS ELECTROCHEMICAL DETERMINATION OF NITRATE AND NITRITE IN AQUEOUS SOLUTION USING SILVER DOPED ZEOLITE-EXPANDED GRAPHITE-EPOXY ELECTRODE

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Since nitrite and nitrate determination is very important for environmental and public health, many electrochemical methods have been developed in the recent years[1–4].

An electrochemical sensor based on Ag-doped zeolite--modified expanded graphite-epoxy composite electrode was evaluated for a new alternative of simultaneous nitrite and nitrate quantitative determination in aqueous solutions. Cyclic voltammetry was used to characterize the electrochemical behaviour of the electrode in the presence of individual and mixture of nitrite and nitrate anions in 0.1 M Na_2SO_4 supporting electrolyte. The linear dependences of current versus nitrate and nitrate concentrations were obtained for the concentration ranges of 1–10 mM for nitrate and 0.1–1 mM for nitrite using chronoamprometry and multiple pulse amperometry procedures. The comparative assessment of the electrochemical behavior of individual and mixture anions on this modified electrode allowed determining the working conditions for the simultaneous detection of them. The proposed sensor was applied in water samples and the results were in agreement with those obtained by comparative method.

This work demonstrated that using multiple pulse amperometry for the Ag-doped zeolite-modified expanded graphite-epoxy composite electrode presents a great potential for simultaneous detection of nitrite and nitrate from water.

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OP-22
COMPLEX STUDY OF DINITROBENZENES ELECTROREDUCTION MECHANISM BY ELECTROANALYTICAL AND COMPUTATIONAL METHODS

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A complex of experimental (cyclic voltammetry (CV), chronoamperometry (CA), electrolysis at controlled potential (ECP)) and theoretical methods (digital simulation, quantum chemical calculations) was used to study the mechanism of electroreduction of 1,2-, 1,3-, and 1,4-dinitrobenzenes (DNBs) in DMF in the presence of various proton donors. The kinetics of reactions of intermediate products was also investigated. The reactions of protonation of the radical anions (RAs) and dianions (DAs) were found to be orbital-controlled. A simple and suitable method was proposed for the prediction of protonation rate constants using the reactivity index, which is calculated by using the values of formal potentials of RAs and DAs formation.

Using 1,4-DNB DAs as an example, it was shown that the protonation of the DNB DA is preceded by the formation of complexes with a hydrogen bond between the proton donor and DA, resulting (under the conditions of proton donor excess) in the inversion of the potentials of RA and DA formation. The number of ligands in the associates was determined.

The electroreduction of 2-, 3-, and 4-nitrosonitrobenzenes (NNBs), being important intermediates of reduction of DNBs, was studied. It was found that the main reaction competing with the protonation of the NNB RAs is the dimerization of the latter that affords the corresponding azoxy- derivates. The value of the rate constant for RA dimerization depends on arrangement of functional groups and decreases in the series 2-NNB > 3-NNB > 4-NNB, whereas the protonation rate increases in the series 4-NNB < 3-NNB < 2-NNB.

It was shown by the CV and ECP methods that the electroreduction of 2- and 4-nitrophenylhydroxylamines in aprotic media is accompanied by the protonation of the electrochemical reaction product with the starting compound to form nitroaniline and nitrophenylhydroxylamine anion. The comparison of the electrochemical and quantum-chemical calculation data suggests that the first step of the transformation considered is the elimination of the hydroxide anion from the RAs of nitrophenylhydroxylamines.

OP-23
ACCURATE CALCULATION OF VOLTAMMETRIC CURRENT BY INFINITE SERIES SOLUTION

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Current–potential curves (*I-E*) represent an essential analytical signal in linear sweep voltammetry, LSV. Mathematical formulation of *I-E* dependences is based on the solution of the system of parabolic differential equations, PDR, different for various electrochemical mechanisms in the composition of initial and boundary conditions. PDRs are describing the concentrations of the reduced *R* and oxidized *O* forms and, prospectively, the concentrations of further species participating in the overall electrochemical mechanism. Despite its high value, but due to their complexity, there still have not been known any analytical functions describing various electrochemical mechanisms in LSV. On the other hand, miscellaneous numerical solutions have been described, *e.g.* in the form of integral equations[1,2] or difference equations employed in digital simulation techniques[3–5]. The only known analytical solutions have been obtained using infinite series[2,6,7]. However, corresponding infinite series do not converge in the most desired potential region close to the maximum peak current, which is basic for quantitative analysis. In this work, new ways of the series transformation are exemplified, which transform diverging or very slowly converging series into converging sequences for several mechanisms containing irreversible charge transfer. Calculated results are accurate in a broad potential range including the potential regions where the original series are not converging. Two different potential scales are used: dimensionless as well as dimensional one (in milivolts); definitions of the scales in both cases are compatible with ref.[2]. Disadvantage of our approach is a relative slow computation and necessity to use arbitrary precision arithmetic[6,7]. Obtained results may be valuable for assessment of accuracy of faster but much less precise techniques, *e.g.* digital simulation.

Financial support from grant APVV-0057-06 is highly acknowledged.

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OP-24
LANGMUIR-BLODGETT FILMS OF NAFION: THE ROLE OF THE THIN FILM IN THE ELECTROCHEMILUMINESCENCE OF $Ru(bpy)_3^{2+}$

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Nafion modified electrodes are typically prepared by cast-coating or spin-coating, however, problems in reproducibility of the analytical performances can be found. Improvements can came from the control of the film thickness and structure, achieved by using the Langmuir-Blodgett (LB) technique. The characterization of LB-Nafion coated electrodes by voltammetry and epifluorescence microscopy[1], demonstrated the compactness of the Nafion LB films as well as the homogeneity of the distribution of the probe incorporated in the film, even when the film is as thin as 2 nanometers. In the present work, we apply electrochemiluminescence (ECL) with the $Ru(bpy)_3^{2+}$ redox probe[2] in LB-Nafion coatings, deposited onto transparent ITO (indium-tin oxide) electrodes using tertiary amines as the coreactant. The study is focused on understanding the role of the LB film on the ECL emission, discriminating between luminescence generated by reactions which take place inside the Nafion LB-film from those occurring at the polymer/solution interface. Finally, examples of application of ECL with LB-Nafion modified electrodes to the analysis of amines of pharmaceutical and toxicological interest are presented.

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OP-25
SUPPORTED PHOSPHOLIPID BILAYERS, THEIR FORMATION AND TRANSPORT ACROSS THEM

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Various inorganic and organic compounds, nutrients, waste materials, *etc.*, must be transported across the cell membrane into or out of the cell or of various sub-cellular structures. The real membranes are mainly composed of phospholipids, however, they contain a wide variety of biological molecules, primarily proteins and lipids, which take part in many cellular processes, such as ion channel conductance, cell signalling, *etc.* To elucidate such transport processes, synthetically prepared model phospholipid bilayers (PLBs) are utilized, in the form of black membranes (*e.g.*, on porous materials), vesicles or supported membranes[1–4], with ion channels incorporated (either artificially synthesized or obtained from real living cells, *e.g.* protoplasts). Some electrochemical methods (Electrochemical Impedance Spectroscopy (EIS), voltammetry, *etc.*) have been used to study the PLBs formed and the transport of charged particles across them. Porous polycarbonate membranes, placed between the two arms of a glass U-shaped cell and special polyethylene tube "inserts" have served as supports for the formation of lecithin bilayers. The systems described have been found to be suitable for incorporation of ion channels, as demonstrated by the experiment with the Valinomycin ionophore. Another type of a supported PLB has been formed on the surface of a glass capillary filled with agar. The lecithin PLBs within the pores of a polycarbonate membrane, with or without ionophores, can be simulated by relatively simple electric equivalent circuits composed of resistors and capacitors. A quite stable phospholipid membrane is formed within ca. 1 hour after immersion in a KCl solution[5]. The time variation corresponds to an increase in the membrane capacitance, *i.e.*, to thinning of the lipid structure[1].

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OP-26

VOLTAMMETRIC DETERMINATION OF PICRIC ACID USING SILVER AMALGAM PASTE AND CARBON PASTE ELECTRODE.

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A sensitive voltammetric method was developed for the determination of picric acid at a silver amalgam paste electrode (AgA-PE) (ref.[1]) in Britton-Robinson buffer and the results were compared to that at carbon paste electrode (CPE). Under the optimal conditions, a linear response at AgA-PE was observed over the 2×10^{-7}–1×10^{-4} M picric acid concentration range examined, with $R = 0.9976$ and a determination limit of 5.6×10^{-8}M. More sensitive results were obtained using accumulation time (t_{acc}) and accumulation potential (E_{acc}). A highly stable response, with a relative standard deviation (RSD) of 2.4%, was observed for 45 repetitive measurements. The picric acid also showed good response at CPE in the concentration range of 2×10^{-6}–1×10^{-4}M with $R = 0.9999$ and determination limit of 4.7×10^{-7}M. There was no accumulation of picric acid found at CPE. A highly stable results were also obtained at CPE with RSD of 1.1% ($n = 45$). Such a highly stable electrochemical response at both electrodes showed that there was no apparent surface passivation. The method was successfully applied for the direct determination of picric acid in drinking and river water.

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OP-27

THE ELECTROCHEMISTRY OF HYDROGEN SULPHIDE IN ROOM TEMPERATURE IONIC LIQUIDS (RTILs)

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Room temperature ionic liquids (RTILs) can be defined as compounds composed entirely of ions, generally a bulky cation and an inorganic anion, existing in the liquid state at 298 K. RTILs have a very low volatility and high thermal stability and can survive temperatures above 453 K, so experiments at high temperatures can be performed without any solvent degradation or reaction with other species in solution[1]. Ionic liquids have a wide electrochemical window which allows experiments to be performed that are normally out of the range of traditional solvents, and they have a high intrinsic conductivity so no supporting electrolyte is required[2]. One of the limitations of the use of RTILs is the effect of water. Water is considered to be one of the most significant impurities in RTILs as it is ubiquitous, and even hydrophobic RTILs absorb some from the atmosphere. Work has shown the extent of water uptake of several RTILs, as well as its effect on the electrochemical window of ionic liquids. This provides information to aid the selection of RTILs as solvents for electrochemical experiments[3].

The focus of this work is on the electrochemistry of hydrogen sulfide (H_2S) gas, which is of major importance in the petrochemical industry, and whose toxicity has necessitated the development of monitoring devices. Separation of H_2S from petroleum refinery and coal gasification processes presents a continuing challenge for clean, reliable operation in the petrochemical industry, which generally implements traditional separation technologies such as distillation, adsorption and stripping, and extraction[1].

H_2S detection in RTILs presents an insight into the voltammetry of gases in ionic liquids such as high solubilities as well as other interactions at the electrode/solvent interface[1,4], and represents a new phase of gas detection whereby gas sensors are not limited by factors such as temperature and pressure.

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OP-28

FROM D.C. POLAROGRAPHIC PRESODIUM WAVE OF PROTEINS TO ELECTROCHEMISTRY OF BIOMACROMOLECULES

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History of electrochemistry of proteins and nucleic acids will be briefly reviewed. The ability of proteins to catalyze hydrogen evolution at Hg electrodes was discovered almost 80 years ago in J. Heyrovský's laboratory[1]. This phenomenon was not sufficiently appreciated for several decades. Recently it has been shown that using constant current chronopotentiometric stripping (CPS) with hanging mercury drop, solid amalgam or Hg-film electrodes the CPS peak H is obtained with nanomolar concentrations of peptides and proteins[2–12]. This peak is derived from the presodium wave but it has some new properties useful in protein research. It is sensitive to changes in protein structures and to protein redox states, representing a new tool for protein analysis applicable in biomedicine. Electroactivity of nucleic acids was discovered about 50 years ago[13–16]. Electrochemistry of DNA and RNA is now a booming field because of its potential use in sensors for DNA hybridization and DNA damage. Quite recently it has been shown that electrochemistry can be applied also in polysaccharide analysis[17,18].

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OP-29

ELECTROCHEMICAL BIOSENSING DESIGNS FOR ULTRASENSITIVE DETECTION OF BACTERIA

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Nowadays, one of the challenges in food industry, environmental monitoring and clinical diagnosis is the development of methods for rapid detection of payhogenic bacteria to prevent risks of infection, bioterrorism, enteric diseases and economic losses. In this context biosensors play a significant role in the determination of pathogens.

Three electrochemical biosensing designs for the ultrasensitive detection of bacteria will be reviewed in this communication. The first one consists of label-free electrochemical impedance immunosensors for detection and quantification of *Escherichia* coli using self-assembled monolayers-modified gold screen-printed electrodes[1]. A rapid analysis (1 h) of 10 cfu mL^{-1} *E. coli* inoculated river and tap water samples was demonstrated.

The second approach implies the development of disposable magnetic DNA sensors using an enzyme-amplified strategy for the specific detection of a gene related to the *Enterobacteriaceae* bacterial family, based on the coupling of streptavidin-peroxidase to biotinylated *lacZ* gene target sequences[2]. The method was used for the analysis of *E. coli* DNA fragments (326 bases) in PCR amplicons extracted from a cell culture. As low as 2.5 aM asymmetric PCR product could be detected with the developed methodology. Finally, a further approach involved the use of direct asymmetric PCR amplified products for *E. coli* detection at a concentration level of 0.01 cfu mL^{-1} with no need for culture preconcentration steps.

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OP-30
THE ELECTROCHEMICAL ASSESMENT OF HEAVY METALS MOBILITY IN THE RHIZOSPHERE

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The anodic stripping voltammetry (ASV) and electrospray ionization mass spectrometry (ESI-MS) were used for determination of heavy metal complexes with low-molecular-weight organic acids (LMWOAs) in soil solutions sampled from rhizosphere and bulk soil. The electrochemical determination of heavy metals complexes in soil solutions obtained from the rhizosphere part of soil is a reliable and cheap variant for assessment of heavy metals availability. Heavy metals mostly exist in soil solutions in complexes with LMWOAs[1]. The main type of the ligand is oxalic acid mostly exuded by willow or penny-cress[2]. The stability constants and the number of ligands can be calculated from the peak-potential shift[3,4]. For the more detailed investigation of the complexes' structure the ESI-MS was used.

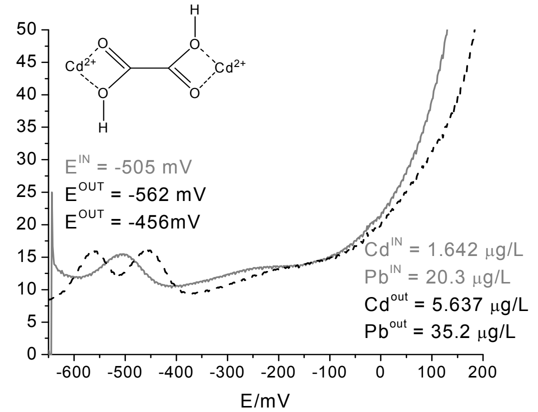

Fig. 1. **The voltammogram** (ASV-HMDE, *vs.* Ag/AgCl/3M KCl, t = 120 s, E_{ac} = –900 mV), and designed structure of one of the cadmium-oxalic acid complexes

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OP-31
ELECTROCHEMICAL CHARACTERIZATION OF REDOX STATE OF HOMOGENEOUS CATALYSTS

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Catalysis by metal complexes is a crucial process in majority of organic reactions. The understanding of molecular details of a catalytic process will lead to the improvement of the existing technology as well as development of new processes. In many cases an oxidation state of a catalyst changes rapidly during the process depending on the composition of the reaction mixture. Cyclic voltammetry is a simple and useful tool to be applied for following the oxidation state changes.

We have demonstrated that hydrogen peroxide and *t*-butyl hydroperoxide used as oxidants in a water solution cause the oxidation of iron catalyst (Fe^{II}→Fe^{III}) whereas in acetonitrile the reduction of catalyst (Fe^{III}→Fe^{II}) by HOOH and *t*-BuOOH, respectively occurs[1,2]. This is also the first reported case when HOOH acts as a reductant in electrochemical catalytic systems. The subsequent research has shown that during the voltammetric measurements of $[Co^{III}(acac)_3]^{3+}$ in the presence of hydrogen peroxide the electrochemical catalytic currents of HOOH acting both as an oxidant and a reductant occur in the one full scan[3]. Using cyclic voltammetric technique we have also shown that $[Mn^{II}(bpy)_2]^{2+}$ complex activates dioxygen for the oxidation of limonene, only when it has been previously oxidized to Mn^{IV} complex[4].

The presented results indicate the usefulness of voltammetric measurements in investigations of mechanisms of catalytic processes.

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OP-32

THE IMPORTANCE OF POLAROGRAPHY IN STUDIES OF THE ELECTRON TRANSFER COUPLED WITH THE CLEAVAGE OF CARBON-HALOGEN BOND

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The study of the reductive cleavage of carbon-heteroatom bond in halogenated organic compounds is proposed. The chlorinated triazines[1], chlorinated dicarboximides[2,3] and halogenated benzonitriles[4] undergo different reduction mechanism according to the solvent and the presence of proton donors or complexing ligands. The half wave potentials of DC polarographic wave shift towards more negative values in the order I > Br > Cl. The location of the first reduction wave is controlled by the bond dissociation energy, which is in agreement with the reduction of halogenated compounds in the literature[5,6]. After the cleavage of carbon-halogen bond the aryl radical can either undergo the electron transfer in the ECE pathway or in DISP pathway, followed by the protonation of resulting aryl anion; or abstract the proton in hydrogen atom transfer (HAT) mechanism[7]. The reduction mechanism of halogenated benzonitriles involves their self-protonation. The overall one electron reduction process in aprotic media is changed at the presence of strong proton donor to the two electron mechanism.

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OP-33

COUPLING OF SCREEN-PRINTED ELECTRODES AND MAGNETIC BEADS FOR RAPID AND SENSITIVE IMMUNODETECTION OF POLLUTANTS

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In this study an electrochemical immunoassay, based on a direct competitive assay, was developed using magnetic beads as solid phase and carbon screen-printed electrodes as transducers for the detection of sulphonamides. Magnetic beads coated with protein A were modified by immobilization of specific antibodies and then the competition between the target analyte and the corresponding analyte labeled with the enzyme was performed; after the immunosensing step, beads were captured by a magnet onto the working surface of a screen-printed electrode for the electrochemical detection[1].

Alkaline phosphatase was used as enzyme label and differential pulse voltammetry as fast electrochemical technique. Calibration curves demonstrate that the developed immunomagnetic sensor was able to detect sulfonamide compounds in standard solutions at low concentrations (sub-ppb level).

The developed electrochemical immunoassay was coupled to solid phase extraction for the analysis of these compounds from honey samples.

The authors thank Prof. M. Franek to have kindly provided antibodies against sulphonamides and the corresponding tracer.

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OP-34

ELECTRODES MODIFIED WITH POLYMER-METAL NANO- AND MICROCOMPOSITES

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Several approaches to the synthesis and/or electrodeposition of polymer-metal composites are compared. Two polymers: polyaniline and polypyrrole and three metals: gold, silver and copper were employed. The polyaniline based composite materials with silver and gold were chemically synthesized at the nitrobenzene/water interface. The aniline monomer was present in the nitrobenzene phase while the oxidizing agents (either gold (III) or silver (I)) were dissolved in water. Formation of polypyrrole with metallic inclusions was carried out similarly; at the interface between the aqueous phase and an organic solution. A variety of the polymer-metal composites were obtained in both polymer systems. For the electrode modification purpose these composites were mechanically transferred to the electrode surface.

Direct deposition of polymer-metal composites on the electrode surfaces were accomplished using further two methods. In one, the voltammetry and amperometry in one solution was employed thanks to the kinetic limitation to the reduction of the metal ion. In the second one, the electrode was dipped in a series of solutions to execute the electroless deposition.

The obtained composite materials and the modified electrodes were characterized by cyclic voltammetry, scanning electron microscopy, and Raman spectroscopy.

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OP-35

DEVELOPMENT OF A SQUARE-WAVE CATHODIC ADSORPTIVE STRIPPING VOLTAMMETRIC METHOD TO ASSAY OF TELMISARTAN IN PHARMACEUTICAL PREPARATIONS AND BIOLOGICAL SAMPLES

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High blood pressure is quantitatively the largest single risk factor for premature death and disability due to its high prevalence in human health all over the World. Telmisartan (TS), Fig. 1, is an angiotensin II receptor antagonist (ARA II) widely used in the treatment of hypertension[1,2].

Many analytical techniques for the determination of TS were described[3–7]. However, these methods need expensive equipment and are time-consuming, and they exact rigid experimental conditions. A simple and rapid method for detecting TS that requires no such procedures is, thus, highly desirable from a practical viewpoint.

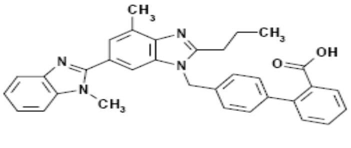

Fig. 1. **Chemical structure of Telmisartan**

In this study, a sensitive, simple and reproducible voltammetric stripping method was developed for the determination of TS in different samples. The method was based on a sensitive reduction peak of TS at –1.449 V *vs.* Ag/AgCl reference electrode in a Britton-Robinson buffer at pH 10.5. Linear concentration range was found as 5.62×10^{-10} M to 2.75×10^{-8} M when optimum preconcentration potential and optimum preconcentration time were applied as –0.45 V and 180 s respectively. Limit of detection and limit of quantitation of the method were calculated to be 3.26×10^{-11} M (16.78 ng L^{-1}) and 1.08×10^{-10} M (55.58 ng L^{-1}) respectively. The proposed method was used for the determination of TS in different samples. The precision was excellent with relative standard deviations (*n* = 5) of 0.79 %, and 1.39 %, concentrations in linear range of real sample analysis of two different drugs.

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OP-36

STRIPPING COULOMETRY DETERMINATION OF LEAD AND MERCURY AT SCREEN-PRINTED ELECTRODES

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One of the methods of stripping coulometry (the so-called standardless combined electrochemical method[1]) is the technique, based on calculation of the quantity of electricity Q_∞, which corresponds to the whole substance convertion, using the following expression

$$Q_\infty = \frac{Q_t}{1-10^{-kt}} \tag{1}$$

where Q_t is the quantity of electricity which corresponds to the substance convertion during the electrolysis time *t* and *k* is the coulometric constant of electrochemical cell.

In accordance to the formula for coulometric constant

$$k = \frac{DS}{\delta V} \tag{2}$$

the value of the constant depends on diffusion coefficient D of analyte ion, surface area S of the working electrode, solution volume V and diffusion layer thickness δ. The largest ratio S/V corresponds to the largest extent of analyte extraction from solution during electrolysis. Application of screen-printed cells allows to minimise the solution volume up to 50 µl, the surface area of working electrode being usually 5–10 mm^2.

Method of determination of coulometric constants of screen-printed cells was proposed. The method is based on dependence of the value of quantity of electricity Q_t (or the value of analyte ionisation peak area S_t, which is directly proportional to Q_t) in function of electrolysis time. The value of coulometric constant k is calculated (numerically or graphically) using the formula:

$$k = -\frac{1}{t}\lg\left(1 - \frac{Q_t}{Q_\infty}\right) \tag{3}$$

Values of Q_t and Q_∞ are found from the dependence of stripping current on electrolysis time.

Using the proposed technique the values of coulometric constants for Pb^{2+} and Hg^{2+} ions at graphite- and gold-based electrodes, correspondingly, were obtained.

The dependences of coulometric constants on solution volume and independences of the constants on analyt concentration were established.

The method was tested using standard additions method.

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OP-37
METAL NANOPARTICLE MODIFIED BORON DOPED DIAMOND FOR USE IN ELECTROANALYSIS

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Metal nanoparticle modified boron doped diamond (BDD) has been used in the electroanalysis of a number of inorganic and organic analytes. This simple electrochemical surface modification has enhanced the sensitivity and analytical ability of BDD effectively and consistently, as reported in a number of publications by our group.

Recently BDD has been utilised as a substrate electrode in the deposition of Bi (ref.[1]), Sb (ref.[2]) and Ni (ref.[3]). The Bi and Sb modified BDD electrodes were used for the determination of Pb(II) and Cd(II). Both metals allowed for the detection of Cd, otherwise unobserved at the bare BDD, when simultaneously deposited with Pb. The Bi modification particularly enhanced analysis, with nanomolar detection limits observed.

Modification of BDD by Ni nanoparticles has recently been reported and was used in the electrocatalytic oxidation of simple organic molecules, namely ethanol and glycerol[3]. The Ni-BDD has shown improved electroanalytical ability compared to a bulk Ni electrode, and offers a simpler alternative to implantation of Ni into the BDD that has previously been reported[4].

The low capacitance of BDD makes it an ideal substrate for sensitive dynamic electroanalytical experiments. The metal nanoparticle modification of BDD offers a simple yet effective approach to enhancing the electroanalytical ability of the relatively unexplored electrode material. As such the area has much potential for further research with respect to alternative modification and analytes.

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OP-38
REACTIVE CARBON PASTE ELECTRODE FOR THE DETECTION OF BIOLOGICALLY IMPORTANT SPECIES

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Vitamin B_{12} is an important species in human physiology with monitoring required since deficiency causes pernicious anemia and neuropathy. The most common requirement for the analysis of vitamin B_{12} is in the quality control of pharmaceuticals (tablets or injection), blood plasma serum and milk product of infants.

In this contribution a simple, sensitive and highly selective method for the detection of vitamin B_{12} is presented. A carbon paste electrode has been constructed with *trans* 1,2-dibromocyclohexane (DBCH) acting both the carbon particles binder as well as reactive material facilitating the electrocatalytic detection of the target species. The detection is based on regeneration of Co(II) electrochemically prepared from Co(III) where regeneration proceeds after reaction Co(I) with DBCH. A detection limit of 8.5×10^{-10} M based on 3σ was achieved. The method was successfully used for the quantification of Vitamin B_{12} in pharmaceutical products.

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OP-39
ELECTROCHEMISTRY ON MULTI -WALLED CARBON NANOTUBE FILMS

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Vertically aligned multi-walled carbon nanotubes (MWCNT) were selectively produced on silica substrate by the procedure of chemical vapour deposition using either acetonitrile (ACN) or benzene (BZ) as carbon sources and ferrocene ($FeCp_2$) as catalyst[1]. Scanning electron microscopic images reveal that the packing organization of the aligned CNT on the silica substrate, and thus the degree of disorder of the produced MWCNT films, differs considerably. Namely, MWCNT films produced upon decay of BZ seem to be more “disordered” compared to MWCNT produced upon decomposition of ACN, which appear to be rather “ordered”[2].

In order to examine the prospective application of MWCNT films as working electrodes for the detection of electro-active compounds in organic solvent media, the techniques of cyclic voltammetry and electrochemical impedance spectroscopy were employed[3]. $FeCp_2$ was selected as the suitable electro-active substance for probing the fabricated MWCNT films in ACN. The extracted results were compared with those obtained on conventional glassy carbon (GC) electrode. The half-wave potential of the $FeCp_2^{+/0}$ couple shifts positively and the peak current remarkably increases on MWCNT films compared to the GC electrode. Anyhow, the heterogeneous electron transfer rate constants demonstrate that the electron transfer process is faster on GC compared to the electron transfer procedure occurs on MWCNT films. Furthermore, among the different MWCNT films investigated, those produced upon decay of BZ seem to be better capacitors, most probable due to their higher active surface area as well as to their small film thickness. It is, therefore, obvious that the high degree of disorder, which occurs on these MWCNT films, plays an important role for the increase of their effective surface area, and thus their capacitance. It is very interesting that the less-ordered MWCNT films provide the greater charge transfer resistance.

The findings of the present work demonstrate the successful detection of $FeCp_2$ at the fabricated MWCNT films verifying that MWCNT films hold promising and important applications in electrochemistry.

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OP-40
SOFT INTERFACES FOR DNA HYBRIDIZATION DETECTION

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DNA recognition, based on its hybridization with immobilized oligonucleotide probes, has a particular interest during the recent years, with a potential for a variety of applications, including drug discovery, study of gene expression, screening of genetic material for mutations, investigation of the molecular basis of infectious diseases, and sequencing of particular genes of interest among complex DNA samples. Direct (label-free) electrochemical detection of a hybridization reaction represents a very attractive approach for detecting bioaffinity interactions. Such a route can be greatly accomplished by monitoring changes in electronic or interfacial properties accompanying the binding event. This approach greatly simplifies the sensing protocol, because it eliminates the need for the indicator addition/association step. Moreover, the reagentless manner offers an instantaneous detection of bioaffinity complex formation and therefore the real-time monitoring of binding.

Being models of a biological membrane, soft interfaces possess unique electrochemical properties suitable for direct transduction of bioaffinity interactions. Layers of amphiphiles supported by solid electrode are sensitive for affinity binding events at their surface. Alternatively, the ion transfer across the interface between two immiscible electrolyte solutions can be affected by the interfacial bioaffinity interactions.

The uniform layers of water-insoluble surfactants or functional alkylthyols were formed as a result of self-assembling at solid electrode support. It was shown that layers are sensitive for binding events on their surface and can be used as transducers for affinity interaction detection[1].

In parallel route of research, it was suggested to use oligonucleotides modified by hydrophobic alkyl linkers as probes for hybridization with DNA targets. The setup based on ITIES supported by gel onto common disposable graphite screen-printed electrode allowing thermodynamic controlled ion transfer of organic cathions from organic into aqueous phase was proposed. The adsorption of different DNA probes onto ITIES was observed with electrochemical methods. The increase of conductivity has been observed in impedance spectra after hybridization between different DNA probes and targets[2]. The sensitivity of the system allowed determining the single mismatch in target sequence in optimized conditions.

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OP-41

DISCOVERY OF TWO-DIMENSIONAL CONDENSATION OF NUCLEIC ACIDS COMPONENTS AT THE MERCURY ELECTRODES – 40 YEARS' HISTORY

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In 1965 one of us (VV) has discovered, that purine and pyrimidine derivatives currently occuring in nucleic acids posses an extraordinary high ability of self-association at the electrode surface and can form there by a two-dimensional condensation a monomolecular self assembled monolayer, a compact film[1,2]. By this high condensation ability nucleic acid bases differ from most of the other purine and pyrimidine derivatives which currently do not occur in nucleic acids. This property was probably significant for the origin of life at the earth[3]. For the time being it is not known why just only a restricted number of purine and/or pyrimidine derivatives show the tendency to self-association. The 2D condensation of nucleic acid bases, nucleosides and nucleotides takes place not only at the mercury surface, but at the smooth surface of single crystal metal electrodes and/or mercury film electrodes as well[4,5]. On the other hand the 2D condensation was not observed at polycrystalline electrodes with rough surface. Similarly with polymeric DNA and/or polynucleotides the 2D condensation was not observed up to know. However, recently we have found that 2D condensation can be observed with certain homopyrimidine oligodeoxynucleotides[6] at negatively charged mercury electrode surface. DNA adsorption at the electrode surfaces is of fundamental interest for the development of DNA-based biosensors[7].

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OP-42

A STUDY OF THE FABRICATION AND ELECTROCATALYTIC ACTIVITY OF CARBON BASED NANOMATERIALS

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Fluorescent semiconductor nanocrystals (such as CdSe, CdTe and PbTe, *etc.*) have been paid great attention due to their unique optical and biochemical features. However, heavy metals are essential elements in these conventional semiconductors, which are under-utilized due to concerns about their toxicity, stability and environmental hazard. Therefore, the search for benign nanomaterials with similar optical properties has become an urgent challenge. Recently, a new type of visible substitute which is exclusively based on carbon has been proposed. These environmentally-friendly carbon nanoparticles (CNPs) have been prepared by laser ablation of graphite[1], electrochemical oxidation of graphite[2], proton-beam irradiation of nanodiamonds[3] and so on.

We have prepared fluorescent CNPs by a microwave pyrolysis method. This clean, cheap, and convenient route shortened the reaction and represents a potential advancement for large-scale industrialization. The abundant surface traps and functional groups endowed them with bright, stable luminescence and excellent water dispersion. The rlectrochemiluminescence behavior and mechanisms were studied in detail. Coupled with their low cost, low cytotoxicity, and ease of labeling, promising applications in biological labeling and biosensors are envisioned.

A hybrid material based on Pt nanoparticles (Pt NPs) and multi-walled carbon nanotubes (MWNTs) was fabricated with the assistance of PEI and formic acid. The cationic polyelectrolyte PEI not only favored the homogenous dispersion of carbon nanotubes (CNTs) in water, but also provided sites for the adsorption of anionic ions $PtCl_4^{2-}$ on the MWNTs' sidewalls. Deposition of Pt NPs on the MWNTs' sidewalls was realized by in situ chemical reduction of anionic ions $PtCl_4^{2-}$ with formic acid. The hybrid material was characterized with TEM, XRD and XPS. Its excellent electrocatalytic activity towards both oxygen reduction in acid media and dopamine redox was also discussed.

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OP-43
CARBON PASTES IN ANALYSIS OF ORGANIC COMPOUNDS

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Carbon paste electrodes in electroanalysis of oxidizable organic compounds are used for more than half a century[1,2] and present an independent and inexpensive alternative to more frequently used separation or spectrophotometric techniques. The lower selectivity of voltammetric methods when analyzing environmental or other complex samples could be overcome by utilizing electrochemical detectors in HPLC on the basis of carbon pastes where the pastes consisting of spherical microparticles of glassy carbon could be used even in media with high content of organic modifier as *e. g.* methanol or acetonitrile where the pastes from classical spectrographic carbon quickly decompose[3]. The use of carbon paste electrodes in analysis of organic compound will be documented on selected examples of environmental and pharmaceutical applications[3]. Attention will be paid both to batch voltammetric methods and to HPLC with electrochemical detection of submicromolar concentrations of various important biologically active organic compounds.

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OP-44
PREPARATION, CHARACTERIZATION AND APPLICATION OF CHITOSAN STABILIZED GRAPHENE COMPOSITE AS ELECTRODE MATERIAL IN ELECROCHEMICAL DETERMINATIONS

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Graphene is a new member to the family of carbon nanoscaled materials[1] and is used in many applications due to the intrinsic unique mechanical and electronic properties the material possesses[2–4]. Biopolymer chitosan is a natural polysaccharide which is widely distributed in the exoskeleton of crustaceans, fungal cell wall, and other biological materials[5].

In this report, chitosan stabilized graphene composite (Chitosan-Graphene) was synthesized by a together-blending and *in-situ* chemical reduction method. The molecular structure and morphologies of the resulting composite was studied and characterized by UV-Vis, FT-IR, Raman and SEM techniques. With chitosan acting as stabilizer and dispersant, Chitosan-Graphene composite can be dispersed well in water ($\mathrm{pH} > \mathrm{p}K_{\mathrm{a,\,chitosan}}$). The composite electrode material showed electrocatalytic effect in studying redox reactions of ascorbic acid and H_2O_2. Chitosan-Graphene is also biocompatible material to efficiently immobilize enzymes. Biocomposite of Chitoasn-Graphene-GOD demonstrated good bio-sensing behavior for determination of glucose.

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OP-45

NANOSTRUCTURED CATALYTIC ELECTRODES FOR LOW-TEMPERATURE FUEL CELLS: ACTIVATION OF REACTIVE SITES THROUGH MODIFICATION WITH ULTRA-THIN FILMS OF METAL OXO SPECIES

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Platinum-based systems are so far the most active and practical electrocatalysts for the reduction of oxygen and oxidation of fuels (methanol, ethanol) in acid media. A common path to enhance reactivity of Pt involves its nanostructuring to produce catalysts of high surface area and dispersion. Further optimization has been achieved through the formation of bi- and trimetallic alloys such as Pt-Co (oxygen reduction), Pt-Ru (oxidation of methanol), and Pt-Sn (oxidation of ethanol). Efficient electrocatalytic systems often utilize robust large-surface-area metal oxides which are capable of not only separating physically metal particles but also interacting with them thus affecting their chemisorptive properties. The ideal matrix should also be reactive towards the inert reactant studied or its reaction intermediates. For example, tungsten oxide has been demonstrated to activate Pt via hydrogen spillover and through the formation of highly conductive W-oxide bronzes (which are reactive towards hydrogen peroxide (oxygen reduction) or adsorbed CO (methanol oxidation) intermediates. Heteropoly tungstic and molybdic acids ($H_3PW_{12}O_{40}$ and $H_3Mo_{12}O_{40}$), which are analogous to the parent hydrated oxides (WO_3 and MoO_3), exhibit analogous properties and form monolayers on metal nanoparticles. For example, the presence of the polyoxometallate monolayer on platinum results in the partial suppression of the interfacial formation of PtOH/PtO oxides (that are inhibiting in the reduction of oxygen). During oxidation of ethanol, a remarkable increase of electrocatalytic currents has been observed after modification with polyoxometallates. The presence of metal oxo species in the vicinity of platinum shall lead to the changes in electronic structures of platinum and thus weaken the adsorption force towards bonding carbon monoxide. Further, fairly efficient electrocatalytic systems utilizing tungsten oxide modified carbon-supported $RuSe_x$ nanoparticles or cobalt protoporphyrin reactive sites, have been developed for oxygen reduction. It is reasonable to expect that, while $RuSe_x$ or metaloporphyrin initiates the electrocatalytic reduction of oxygen, WO_3 facilitates decomposition of the undesirable hydrogen peroxide intermediate and makes the overall reduction closer to the 4-electron process. Synchrotron X-ray Photoelectron Spectroscopy (XPS) experiments, which allow us to comment on the electronic modification of electron core levels caused by presence of adsorbed WO_3, clearly show that the WO_3 is not only adsorbed on the catalyst's surface but it also tends to interact electronically with $RuSe_x$ catalytic centers. Similar XPS measurements have been done with the metal oxide or polyoxometallate modified noble metal nanoparticles and their alloys.

OP-46

ELECTROCHEMICALLY ASSISTED INJECTION FOR CAPILLARY ELECTROPHORESIS – MASS SPECTROMETRY STUDIES OF NEUTRAL ANALYTES

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The separation of neutral analytes by capillary electrophoresis (CE) is conventionally realized by adding surfactants which form charged micelles interacting with the analyte species. However, this so-called micellar electrokinetic capillary chromatography (MECC) has serious limitations with respect to direct coupling with mass spectrometry (MS).

In this contribution we suggest an alternative concept for CE separations of neutral analytes offering full compatibility with MS detection. The new approach is based on the electrochemical conversion of analyte species during the injection into the separation capillary. This concept is termed electrochemically assisted injection (EAI) (ref.[1]).

Several ferrocene derivatives including ferrocene, ferrocene methanol, decamethylferrocene and octamethyl-5,5′-di-(2-pyridyl)ferrocene were studied using an acetonitrile-based buffer. EAI enabled the separation and sensitive MS detection of the formed cationic oxidation products. In addition, EAI-CE-MS was used as a tool for mechanistic studies of oxidation processes. In order to optimize the protocol for EAI additional investigations were undertaken using scanning electrochemical microscopy (SECM). The SECM experiments were performed using an arrangement where the conventional probe electrode was replaced by a fused silica capillary probe with an integrated microcylinder electrode. This configuration was employed to characterize the mass transport situation corresponding to the respective EAI protocols.

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OP-47

MODERN ELECTROCHEMICAL TECHNIQUES FOR THE ANALYSIS OF REACTION MECHANISMS IN CONDUCTING POLYMERS

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The modern techniques of spectroelectrochemistry are used for the ananlysis of the charge injection into conducting polymers. It is well accepted in the scientific community, that polyaniline consists of a linear arrangement of the monomers. Since the early work of Willstätter the phenazine rings have been considered as a part of the polymer chains[1]. The role of the phenazine structure in the stabilization of charged states in polyaniline was studied by *in situ* ESR-UV/vis-NIR spectroelectrochemistry[2] of polyaniline and the copolymers of aniline and a phenazine derivative (3,7-diamino-5-phenylphenazinium chloride, phenosafranine). It is shown that the copolymer can be prepared by electropolymerization the structure of which was confirmed by mass spectrometry and IR spectroscopy. The electrochemistry of polyaniline and its copolymer pointed to preferred stabilization of a polaron pair in the charged states at the initial charge transfer reaction instead of polarons which are formed by equilibrium reaction at higher electrode potentials. A second polaron pair is detected for higher doped states of the polymer films. A mechanism of the formation of charged states in polyaniline and their equilibrium is shown on Fig. 1. It is shown that *in situ* ESR-UV/vis-NIR spectroelectrochemistry is the method of choice to differentiate between polarons and polaron pairs in their potential dependent formation. Thus, by this *in situ* spectroelectrochemical method the influence of the phenazine structure on the formation of polarons in aniline polymers and copolymers can be followed.

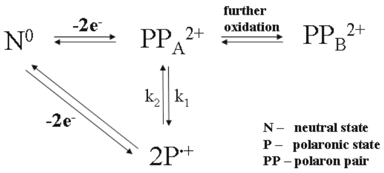

Fig. 1. **Scheme of the formation of charged states upon electrochemical oxidation of polyaniline**

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OP-48

MONOCRYSTALLINE DIAMOND PASTE BASED SENSORS AND MICROSENSORS

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Advanced single-crystal diamond has enabled the development of a wide range of monocrystalline diamond products to meet the exacting requirements of an amperometric transducer. The reliability of the electrical properties of single-crystal diamond is encouraging for research in the electrochemical sensors based on monocrystalline diamond, as well, it proves that the doping of monocrystalline diamond is not necessary which minimizes the time affected for electrode's construction and also simplified the steps adapted for the design of such electrochemical sensors.

Sensors and microsensors based on monocrystalline modified or plane diamond paste were designed and used for analysis and enantioanalysis of analytes of clinical and pharmaceutical importance. The advantages of such sensors over the carbon paste ones are: lower detection limits, higher sensitivities, higher selectivity and lower noise which has as result the improvement of signal/noise ratio value up to 100 times.

Stochastic microsensors were constructed by utilization of porphyrins as active component for sensors' design. These sensors can be reliable used for both qualitative and quantitative analyses.

Applications of these sensors and microsensors in clinical and pharmaceutical analyses will be shown.

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OP-49

SENSORS AND BIOSENSORS FOR MULTICOMPONENT ANALYSIS USING FLOW SYSTEMS

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Multicomponent analysis is essential in process control in fields like clinical and pharmaceutical analysis. Different sensors and biosensors were proposed as detectors in flow injection analysis (FIA) and sequential injection analysis (SIA). Reliability of sensors and biosensors is essential for their selection as detectors in flow systems.

Applications of FIA and SIA/(bio)sensors for multicomponent enantioanalysis and analysis, *e. g.*, L- and D-pipecolic acid, L- and D-captopril, L-T_3, L-T_4 and D-T_4 will be discussed.

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OP-50

COMBINATION OF POTENTIOMETRIC AND AMPEROMETRIC MICROPROBES TO MONITOR THE ELECTROCHEMICAL ACTIVITIES IN CONFINED MICRO-DEFECTS OF COATED METALS

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Active corrosion protection based on self-healing of defects in coatings is a vital issue for development of new advanced corrosion protection systems. However, there is a significant lack of experimental protocols which can be routinely used to reveal the self-healing ability and to study the active corrosion protection properties of organic and hybrid coatings. One of the tools, which allow direct observation of the corrosion activity in the micro-confined defects, is Scanning Vibrating Electrode Technique (SVET). Regrettably, it is only sensitive to charged species and is unable to identify the species detected.

The present work demonstrates how micro-potentiometric and micro-amperometric mapping of different species in electrolyte near the active surface can help the interpretation of SVET data, complementing it. The microcapillary-based potentiometric pH-sensor was used to acquire distribution of OH^- ions during the corrosion processes in artificial micro-defects in pure and inhibitor-doped electrolytes. Concentration of metal ions originated from the active defects was measured by ion-selective microelectrodes as well. The inert metallic microelectrode was employed here to study the distribution of local oxygen concentration near the cathodic and anodic defects. The aluminium and magnesium alloys coated with hybrid sol-gel film were used as model systems to study the healing of artificial defects by different organic and inorganic corrosion inhibitors.

The corrosive process was addressed from the side of the solution. The measurement of the ionic currents in solution permitted to follow the evolution of the process in time and the inhibition kinetics of a soluble inhibitor. The local distribution of pH, metallic cations and dissolved oxygen gave extra information about the corrosion and inhibition process. This can be very useful in studies of self-healing of coatings in defects.

OP-51

POTENTIOMETRY IN GAS PHASE

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In order to yield analytically useful information every potentiometric measurement requires stable and reproducible reference potential. That requirement has to be satisfied for potentiometry performed in liquid or gas phase alike, although two fundamentally different mechanisms lead to formation of the measurable cell voltage. It is shown that the Fermi level of silicon used in insulated gate field-effect transistors (IGFET) provides an exceptionally stable and robust reference potential. A semi-quantitative dependence of IGFET output on partial pressure of the analyte gas is presented.

POSTERS

PP-01

ELECTROCHEMICAL STUDY OF 3-(AZIDOMETHYLENE)DIHYDROFURAN-2-ONE

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Organic azides are important compounds not only in organic synthesis but also in medicine as based molecule for preparation of drugs for HIV positive patients (*e. g.* azidothymidin)[1]. From electrochemical point of view azide group is subject to reduction. In this study we discussed the reduction of 3-(azidomethylene) dihydrofurane-2-one (AZMDF), which occurs in two conformations: (*E*) form and (*Z*) form. These furanoid azides were prepared due to studying of reactivity of α-tosyloxymethylenlactones[2]. Using linear sweep or cyclic voltammetry and elimination voltammetry with linear scan (EVLS) (ref.[3–5]) in connection with a mercury electrode, signals of (*E*) and (*Z*) forms of AZMDF were clearly distinguished. In addition, we optimized experimental conditions to enhance sensitivity of determination of target molecules. The highest reduction signals of both isomers were measured in KCl, but the best distinguishing of both isomers was determined in the presence of borate buffer. While (*E*) form has the highest reduction peak at pH 7.94, (*Z*) form at pH 8.84. The detection limit was evaluated down to 1 mM. It was found by EVLS that the reduction process of azide group is diffusion-controlled process and this process is little dependent on pH.

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PP-02

SIMULTANEOUS DETERMINATION OF ZINC (II), LEAD (II) AND COPPER (II) AT BISMUTH FILM ELECTRODE BY MULTIVARIATE CALIBRATION

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In 2000, a new type of electrode, the bismuth film electrode (BiFE) was proposed as an environmental friendly alternative to mercury film electrode (MFE) for anodic stripping voltammetry (ASV) measurements of heavy metals[1]. Most metals, with exception of copper, form binary alloys with bismuth, and hence, display well defined and undistorced peaks which permit convenient multi-elemental measurements[2]. However, simultaneous determination of Cu (II), Pb (II) and Zn (II) ions using BiFE electrodes is prone to interferences, which can be attributed to the formation of intermetallic compounds (*e.g.* Cu-Zn) and poor resolution between adjacent peaks of Cu (II) and Bi (II), ref.[2–4]. The chemometric tools are useful to solve this kind of drawbacks[5] and thus the use of these tools deserves further research.

This communication reports the simultaneous determination of Pb (II), Zn (II) and Cu (II) ions at low concentration levels (ppb) by square wave anodic stripping voltammetry on a BiFE plated *in situ* at a glassy carbon electrode (GC). Discrete wavelet transform was applied for processing copper and bismuth overlapped peaks, improving the detection limit for Cu (II) ions down to 2 ppb. The construction of multivariate calibration models, based on partial least squares regression (PLS), allowed the simultaneous determination of Pb (II) (in the concentration range 2.5 to 70 ppb), Zn (II) (10 to 120 ppb) and Cu (II) (2 to 15 ppb) ions with prediction errors below 10 %.

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PP-03

ELECTROCHEMICAL BEHAVIOR OF DNA AND RNA HEPTAMERS AT A MERCURY ELECTRODE

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Hairpins play an important role in many biological processes including triplet repeat expansion associated with neurodegenerative diseases (fragile X syndrome, Huntington's disease, Friedreich's ataxia or myoclonic epilepsy)[1]. The shortest and the most stable hairpin is formed by the DNA heptamer d(GCGAAGC) (ref.[2,3]). This sequence can be found in replication origins of phage ϕX 174 and herpes simplex virus, in a promoter region of an *Escherichia coli* heat-shock gene and in rRNA genes. In this study, we studied d(GCGAAGC) hairpin and its RNA analog by means of adsorptive stripping voltammetry. Both DNA and RNA heptamers, adsorbed on mercury electrodes, provided voltammetric reduction signals of adenine and cytosine (A and C) and oxidation signals of guanine (G). The dependences of these voltammetric signals on pH, accumulation time, scan rate and loop sequences were determined. For the resolution of A and C reduction signals and for the evaluation of nature of anodic processes of G signal in both heptamers elimination voltammetry with linear scan (EVLS) was utilized[4–6].

Our results show that EVLS, as a fast, simple, and inexpensive electroanalytical tool, is effective not only for the detection and resolution of A and C bases in oligonucleotides and for the characterization of nature of electrode processes, but also for the sensitive detection of changes in primary and secondary structure of nucleic acids' fragments.

This work was supported by INCHEMBIOL (MSM 0021622412), BIO-ANAL-MED (LC06035) from the Ministry of Education, Youth and Sports of the Czech Republic

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PP-04

VOLTAMMETRIC DETERMINATION OF B_1, B_2 AND C VITAMINS IN PHARMACEUTICAL PRODUCTS

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Vitamins are organic compounds which are required for the normal growth and maintenance of life of animals, including man, who, as a rule are unable to synthesize these compounds by anabolic processes[1]. Most of the vitamins induce reasonable polarographic and voltammetric responses and can be qualitatively as well as quantitatively determined voltammetrically[2–4], without interference resulting from the presence of each of them and other compounds under optimum experimental conditions.

In the work, the cyclic renewable mercury film silver based electrode (Hg(Ag)FE) (ref.[5]) was proposed as a working electrode for B_1, B_2 and C vitamins detection in pharmaceutical products. The Hg(Ag)FE, refreshed before each measurement, demonstrates many properties specific only for the hanging mercury electrode. The preparation of the Hg(Ag)FE electrode is very simple and economically acceptable, it has a very good stability, and the renovation of the surface is easy. The Hg(Ag)FE is characterized by very good surface reproducibility (≤ 2 %) and long-term stability (more than 2 thousand measurement cycles).

Before the measurements realized by staircase, normal pulse and differential pulse voltammetry methods, optimization of the supporting electrolyte composition, preconcentration conditions and other important parameters was done.

The influence of organic interfering substances was done by addition of Tritonu X-100: 5 mg L^{-1} in the case of B_1 vitamin and 60 mg L^{-1} in the case of B_2 vitamin. In the presence of Tritonu X-100 stability of the electrode parameters and repeatability of the signal were tested. Also procedure of Hg(Ag)FE electrochemical conditioning was proposed.

The developed methods were successfully applied and validated by studying the standard substances and various commercially available pharmaceutical products.

The study was supported by the Ministry of Science and Education (AGH Project No. 11.11.160.799).

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PP-05
THE RENOVATED GOLD RING ELECTRODE

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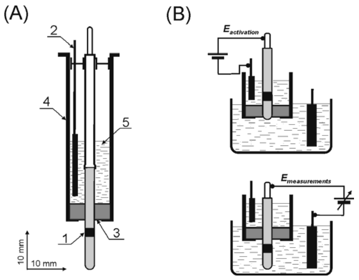
In this preliminary note, a new type of "mercury-free" working electrode − the renovated gold ring electrode (RGRE) − is presented. The only four constituents of the RGRE: a specially constructed gold ring electrode (1), a silver sheet used as silver counter/quasi-reference electrode (2) and a silicon O-ring (3) are fastened together in a polypropylene body (4). The renovation of this electrode is carried out through mechanical removal of solid contaminants and bubbles of the gas (hydrogen) and electrochemical activation in the electrolyte (5) which fills the RGRE body[1,2]. The most important advantages of this construction are: possibility of transfer of the electrode from the activation cell to the measurement cell without any contact with air in the conditions of the minimal distortion of the compact part of the double layer. Excellent repeatability and reproducibility – also in organic samples solutions – were reached in a period of a few weeks, through the renovation of the electrode surface before each measurement.



As it was shown on selected examples, the RGRE exhibits good performance in underpotential deposition stripping voltammetry (UPD-SV) (ref.[3]) applied for the determination of Pb(II) and Cu(II) traces[4] in synthetic solutions with and without surfactants and in certified reference materials. The obtained results confirm that the RGRE may be in the future incorporated into out-of-laboratory sensor systems.

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PP-06
POLAROGRAPHIC STUDY OF THE INTERACTION BETWEEN CUCURBIT[6]URIL AND DIVALENT CATIONS

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The cucurbit[n]uril family (CB[n], n = 5–10) is a group of macrocyclic, pumpkin-shaped compounds comprising n glycoluril units enlaced by methylene groups. They have common properties as two polar "portals" (due to ureido carbonyl groups), a hydrophobic interior, and a modest or low solubility in water that is enhanced if an alkaline or alkaline-earth cation is present. The main difference among them is the diameter, which depends on the number of glycoluril units; they have different recognition properties due to this feature. Although much of the work with CB[n] has been done in supramolecular chemistry with organic compounds[1], there are also researches on their interactions with metals. Some of them deal with the interaction to assemble supramolecular adducts in solid state[2]. Buschmann's group reported the stability constants of several metal complex with CB[5], a homologous of CB[5], and CB[6], either alkaline and alkaline-earth[3] or heavy metals[4].

This work was done using a static drop mercury electrode. In our knowledge, no group has surprisingly studied the interaction between any CB[n] and metal using this electrode. The employed macrocyclic ligand was CB[6], previously dissolved. This study was done with zinc (II), cadmium (II), manganese (II), cobalt (II) and nickel (II) in different supporting electrolytes. We found that the stoichiometry depends on the metal. Their stoichiometry varied from 2:1 to 4:1 (metal:CB[6]). In some cases the complex was electroactive and thus the stability constant can be calculated.

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PP-07
HIGH-STABLE PLANAR SENSORS FOR HYDROGEN PEROXIDE DETECTION BASED ON PRUSSIAN BLUE STABILIZED WITH NICKEL CYANOFERRATE

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Hydrogen peroxide is considered as an important analyte nowadays. It is known as a chemical threat agent and the most valuable marker for oxidative stress[1].

We already reported on Prussian Blue as the most advantageous hydrogen peroxide transducer[2]. The main disadvantage of the Prussian Blue based sensing layers is their inherent instability.

The approach for stabilization of Prussian Blue films with nickel and cobalt cyanoferrates has been already proposed in our laboratory[3]. However, this method involves electrochemical stage which is non-applicable for mass production of sensors.

In this work we proposed a novel method for Prussian Blue films stabilization with nickel cyanoferrate. This procedure is based on open-circuit deposition of Prussian Blue and nickel cyanferrate by analogy with interfacial polymerization[4].

We used screen-printed electrodes (Rusens Ltd.) to simplify the procedure of sensor production and to lower their cost.

The novel method of stabilization Prussian Blue films allows to exclude electrochemical stage and to simplify the procedure of electrodes modification. Analytical characteristics of developed sensors are tested in FIA. The linear calibration range is prolonged over four orders of magnitude of hydrogen peroxide concentrations from 1×10^{-7} to 1×10^{-3} M. The developed sensors display dramatically improved operational stability at continuous monitoring of hydrogen peroxide. Under the constant flow of hydrogen peroxide (1 mM) sensors hold 100 % activity during almost half an hour with subsequent very slow decay.

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PP-08
DETERMINATION OF TRACE ANTIMONY BY ADSORPTIVE STRIPPING VOLTAMMETRY USING CYLINDRICAL MERCURY FILM ELECTRODE

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Antimony and his chemical compounds are very ecotoxic[1]. This element is found in two oxidation states Sb(III) and Sb(V) in environmental, biological and geochemical samples[2]. The toxicological behavior of antimony depends than his oxidation state. Antimony compounds in the oxidation state +3 are more poisonous than those in the oxidation state +5 (ref.[3]).

A variety of voltammetric methods has been proposed for Sb and compounds, including anodic stripping voltammetry (ASV) (ref.[4]) and adsorptive cathodic stripping voltammetry (AdSV) at a hanging mercury drop electrode[5].

In the work a sensitive and selective adsorptive stripping voltammetry for the determination of trace antimony using cylindrical mercury film silver based electrode is presented.

The proposed procedure electrochemical determination of antimony under optimized conditions allows obtain the detection limit as low as 0.17 nM (21 ng L^{-1}) for preconcentration time of 90 s. The method was successfully applied for antimony determination in environmental samples.

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PP-09

STRIPPING VOLTAMMETRIC DETERMINATION OF As(III) IN NATURAL WATER SAMPLES WITH COMPLICATED MATRIX

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Knowledge of the speciation of arsenic in natural water is important because the bioavailability and the physiological and toxicological effects of arsenic depend on its chemical form. Because inorganic compounds of arsenic are more toxic than the organic ones and toxicity of As(III) is higher than that of their pentavalent species procedures of determination of this form are necessary. A number of voltammetric methods for As(III) determination with low detection limit have been recently developed, but only some of them can be used for As(III) determination in the presence of the organic substances commonly present in natural samples such as humic substances and surface active compounds. It is related to the fact that even small concentrations of organic matter often cause a decrease or decay of the arsenic voltammetric signal.

This communication provides a simple and fast procedure for As(III) determination which allows for the analysis of natural samples with complicated matrix containing high concentration of surfactants and humic substances. The proposed procedure is based on the stripping voltammetric method of As(III) determination in the presence of copper and HCl as supporting electrolyte. All experiments were carried out with an μAutolab analyzer and a controlled growth static mercury electrode in the HMDE mode. A three-electrode voltammetric classic cell consisting of an Hg working electrode, a Pt auxiliary electrode and an Ag/AgCl reference electrode.

The interference from matrix of natural samples was drastically decreased by adding Amberlite XAD-7 resin to the sample. The resin is added directly to the voltammetric cell to the analysed sample before the deaeration step and interferents such organic substances are removed from the sample during the deoxygenation step. Therefore the proposed voltammetric procedure is very simple and fast. To obtain the optimal conditions of removing organic matter by adsorption on Amberlite XAD-7 resin composition and concentrations of the supporting electrolyte, the amount of the resin and the time of sample contact with resin were studied. The experiments were performed for synthetic samples containing surface active compounds such as Triton X-100, SDS and CTAB (nonionic, anionic and cationic surfactant, respectively) and humic substances such as humic and fulvic acids. The presented method was successfully applied to the speciation of arsenic in natural water samples and certified reference material. The attractive parameters and the successful application of the elaborated procedure holds great promise for exploiting it for environmental and industrial monitoring of As(III).

PP-10

ELECTROCHEMICAL DEPOSITION – STRIPPING ANALYSIS BY ONLINE ELECTROCHEMICAL FLOW CELL – MASS SPECTROMETRY

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During the last years the Laboratory of Environmental Chemistry is developing a powerful tool for analysis of the intermediates and by-products of electrochemical reactions by electrochemical flow cell coupled directly to an on-line mass spectrometer[1–4]. On-line methods are always preferable in electrochemistry over preparative electrolysis followed by *ex situ* analysis, since they minimize interferences, contaminations, electrode fouling and oxygen penetration. We have introduced a thin radial flow cell equipped with a miniature working electrode. The miniature electrode guarantees minimal uncompensated Ohmic drop within the flow cell, and the very thin layer configuration provides high conversion even for small electrodes at relatively high flow rates.

Recently, we have developed a modified version of the EC/ESI-MS instrument for electrochemical preconcentration, desorption and analysis of analytes by EC/ESI-MS (ref.[5]).

A methodology for on-line preconcentration of analytes and their subsequent electrochemically induced delivery to an on-line electrospray mass spectrometer is introduced. The approach is based on electrodeposition of an active metallic layer, silver deposit in this particular case, subsequent specific accumulation of the target analyte by electrochemical or chemical means onto the active layer, and finally oxidative electrostripping of the conductive layer along with the supported analyte to an on-line mass spectrometer. We demonstrate the new concept by selective electrochemical deposition of homocysteine and other organothiols directly on the working electrode of a miniature flow cell. The same approach was extended to the conjugation of the target analyte (avidin as a test case) to a thiolated ligand (biotin in this case) that was electrodeposited on the silver coated surface. Electrostripping of the silver dissolves the target species and allows their delivery to an on-line ESI-MS.

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PP-11
SIMULTANEOUS DETERMINATION OF PHENOLIC AND AMINIC ANTIOXIDANTS IN LUBRICANT OILS

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This paper deals with the voltammetric determination of synthetic phenolic and aminic antioxidants in lubricant oils applying linear sweep voltammetry. Antioxidants belong to the additives, which prevent the attrition of oils and prolong its lifetime[1,2]. The measurements were carried out using gold working electrode, Ag/AgCl/KCl as reference and platinum wire as an auxiliary electrode in acid medium of sulphuric acid with addition of acetonitrile.

The phenolic antioxidants present in the sample in absence of aminic ones, can be determined directly after their extraction by ethanol. The measurements in mixture of both types of antioxidants in oils are complicated by the fact that the present aminic antioxidants influence the determination of phenolic ones. The results are lower. For the elimination of mentioned interference new method, based on known reaction of aromatic amines with nitric acid to nitrosamine, was evaluated and optimized.

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PP-12
NEW MULTIPURPOSE ELECTROCHEMICAL ANALYZER FOR SCIENTIFIC AND ROUTINE TASKS

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The presented device is a new modernized and improved construction of the analyzer which different versions were developed in our team for past 30 years. In this construction the modern fully integrated chips were applied, dedicated for measurements of low level of the recorded value.

The proposed multipurpose analyzer ensures complete measuring features and may control different electrochemical sensors, such as: different types of mercury film electrodes (Hg(Me)FE) (ref.[1]), renewable solid electrodes[2], microelectrodes, corrosion cells, which are fully integrated with the device. Among other, it is the only instrument which fully supports the Controlled Growth Mercury Dropping Electrode (CGMDE) (ref.[3]). The techniques accessible in the analyzer are: staircase, normal pulse, differential pulse, square-wave, linear sweep voltammetry, stripping voltammetry, chronoamperommetry, *etc.* Numerous measuring parameters in each method may be flexibly chosen, what gives practically unlimited possibilities of the experiment programming. The recorded curve is visualized, stored and may be separately, or as a part of the set of curves, transformed and interpreted in unlimited manner. Different typical and more advanced signal processing procedures are built-in and easy accessible[4–7]. For example, smoothing and baseline correction may be done using various algorithms. Also the procedure which enables quantitative determinations is available – calibration may be done using different strategies.

There are almost unlimited possibilities of application of the analyzer. These are scientific investigations of electrode processes, testing of modern sensors, determination of nonionic surface–active substances and typical routine analysis of artificial, environmental, pharmaceutical samples. Also corrosion processes may be investigated using this system.

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PP-13
RENEWABLE SOLID ELECTRODES – APPLICATIONS IN THE PRESENCE OF DOUBLE LAYER MODIFICATORS

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In stripping voltammetry[1,2] which is widely used in electroanalysis, a hanging mercury electrodes (HMDEs) is usually applied. A characteristic feature of the HMDEs is high rate of adsorption of various surface–active species (SAS) on the mercury surface. This property can be used in analysis of surfactants[3] but also makes it impossible to realize the analy-

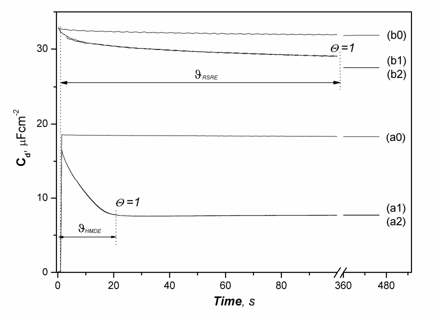

Fig. 1. **C_d–t for HMDE (a0) and RSE (b0) in 10 mM (HNO_3 + KCl);** Curves: (a1) and (b1) after 5 mg L^{-1} Triton X-100 addition, (a2) and (b2) after generation of the new mercury drop (HMDE) and renovation of RSE

sis of non-pretreated samples. This problem does not concern renewable solid electrodes (RSE) because the adsorption time (υ) of SAS on solid electrodes is much longer than in the case of the HMDE, while the effectiveness of renovation is comparable (Fig. 1, ref.[4]).

The proposed approach was verified by the quantitative determination of Pb and Cd ions in CRM water samples, spiked with SAS on a renovated Ag, Au, Ti(C, N) electrodes. It was concluded, that Pb and Cd peaks on the RSE were unaffected by polyethylene glycols in the tested concentration range 0–200 mg L^{-1}. Also SDS and Triton X-100 in concentrations up to 100 mg L^{-1} had marginal influence for the peaks height of both metals. Moreover, in this work the new automatic algorithms of signal processing and quantitative analysis were developed.

The study was supported by the Ministry of Science and Education (AGH Project No. 11.11.160.799).

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PP-14
VOLTAMMETRIC DETERMINATION OF SUCCINYLACETONE BY ESTERIFICATION

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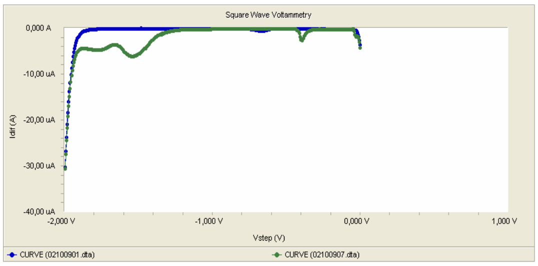

Fig. 1. **The voltammogram of the standard solution of SA after reacted with methyl alcohol in the presence of 0.05 M phosphoric acid** (pH 2)

Succinylacetone (SA, 4, 6-diketoheptanoic acid) is primary diagnostic metabolite for inherited disorder hepatorenal tyrosinemia type I (ref.[1]). Tyrosinemia, type I is a devastating disorder of childhood that causes liver failure, painful neurologic crises, rickets and hepatocarcinoma[2]. In this work a voltammetric determination of SA in amniotic fluid was investigated for assisting the early diagnosis of tyrosinemia type I.

All voltammetric measurements were carried out with a Gamry electrochemical analyzer. A hanging mercury drop electrode (HMDE) was used as a working electrode. Potassium chloride (0.1 M) was selected as supporting electrolyte. The square wave voltammetric operating conditions were as follows: equilibration period: 5 s, voltage step: 0.01 V, pulse amplitude: 0,1 V, frequency: 100 Hz.

Under operating conditions, succinylacetone gave an irreversible reduction peak at –1.68 V *vs.* Ag/AgCl reference electrode. The electrochemical reduction of SA was calculated to proceed with one electron transfer. Linearity range of calibration curve was between 1.23–4.41×10^{-4} M. Limit of detection (LOD) and limit of quantification were calculated as 2.92×10^{-5} M and 9.76×10^{-5} M respectively. This LOD value is inadequate for the determination of succinylacetone in biological fluids. Esterification of succinylacetone with methanol in acidic medium amplified the electroreduction current while producing two peaks as shown Fig. 1. Esterification procedure was useful not only for improved the LOD but also for the extraction of succinylacetone from amniotic fluid.

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PP-15
IMPROVEMENT OF ENZYME BIOELECTROCATALYSIS USING SUBSTRATE CONTAINING ELECTROACTIVE POLYMERS

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Bioelectrocatalysis is the acceleration of electrochemical reactions by biological catalyst[1].

We show the improvement of bioelectrocatalysis using electroactive polymers containing analogues of the enzyme substrates in cases of different enzymes: hydrogenases and cellobiose dehydrogenases from different sources.

The latter having affinity to enzyme active site or its electron-transport chain are expected to provide proper orientation of these biological catalysts. Moreover, the use of highly electroactive artificial substrates is expected to improve electron exchange between the enzyme electron transport chain and the electrode.

Indeed, hydrogenase from *T. roseopersicina* being immobilized over polypyrrole containing viologen groups as substituents displays in average five times improved electrocatalytic activity as compared to the enzyme immobilized directly on carbon surface.

The dramatic effect of using promoters was observed in case of hydrogenase from *D. baculatum*. Where as directly on carbon no bioelectrocatalysis can be observed, immobilization of this enzyme over polypyrrole-viologen resulted in the most active hydrogen enzyme electrode[2].

Cellobiose dehydrogenase from *Myriococcum thermophilum* being immobilized onto carbon screen printed electrodes displays the direct bioelectrocatalysis. Electropolymerized Methylene Green and in particular electropolymerized Methylene Blue promotes dehydrogenase bioelectrocatalysis very efficiently.

We believe that the reported conception will help to involve much more enzymes in efficient bioelectrocatalysis. This would led to elaboration of novel biosensors, enzyme fuel electrodes for biofuel cells and even allow to develop useful systems for specific electrosynthesis.

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PP-16
ELECTROPOLYMERIZATION OF *N*-SUBSTITUTED PYRROLS FOR DEVELOPMENT OF LACTATE AND GLUCOSE BIOSENSORS BASED ON PRUSSIAN BLUE MODIFIED ELECTRODES.

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Entrapment in electropolymerized films remains the most popular electrochemical approach for biosensor fabrication. Effective and inexpensive biosensors for lactate and glucose received by electropolymerization would find wide application in clinical diagnostics, sports medicine, food and agricultural raw materials quality control as well as the control of fermentation processes.

Screen-printed electrodes (Rusens Ltd., Russia) have been used to simplify the procedure of sensor production and to decrease their cost. The working surface of planar electrodes have been modified by Prussian Blue which is known to be the most effective hydrogen peroxide transduser[1]. Lactate oxidase and glucose oxidase were immobilized into conducting polymer films on the surface of planar electrodes modified with Prussian Blue. Different *N*-substituted pyrrole monomers sinthesized by professor S. Cosnier (Grenoble University) were electropolymerized to obtain the conducting polymer[2]. The analytical characteristics of the resulted lactate biosensor in FIA were: the sensitivity of 190±14 mA M^{-1} cm^{-2}, linear dynamic range of 5×10^{-7}–5×10^{-4} M, response time about 30 seconds, high operational stability (more than 100 measurements in FIA). Glucose biosensor has the following characteristics: the sensitivity of 44±4 mA M^{-1} cm^{-2}, linear dynamic range from 5×10^{-6} to 5×10^{-3} M and high operational stability. The application of lactate and glucose biosensors for food quality control (kvass, milk products) has been shown[3].

Highly stable and suitable for multiple use biosensors with a low detection limit may be applied also for the noninvasive lactate and glucose analysis in clinical diagnostics.

The authors are grateful to professor S. Cosnier (Grenoble University, France) for providing samples of N-substituted pyrroles. Financial support by the RFBR grant 06-03-33013-a, INTAS innovation grant 05-10000070429, Contracts of Federal Agency for Science and Innovation №02.512.12.2028 №02.512.11.2326 are greatly acknowledged.

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PP-17

STRIPPING VOLTAMMETRIC DETERMINATION OF METHYLMERCURY IN THE PRESENCE OF INORGANIC MERCURY

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Mercury has been widely recognized as one of the most hazardous of environmental pollutants and a highly dangerous element due to its accumulative and persistent character in the environment and biota. Although inorganic mercury is highly toxic, methylated forms of mercury are even more dangerous since they can be concentrated through the food chain as a consequence of their high solubility in lipids. Methylmercury is the most commonly occurring methylated form of mercury. For these reasons analytical tools for determination of methylmercury at low concentration levels are necessary.

Electrochemical methods require relatively cheap instrumentation, offer low detection limits and often allow for direct determination of the species of interest. Most of the voltammetric procedures for quantification of methylmercury are based on methylmercury reduction to its radical and then its fast reoxidation. Recently a new way of elimination of Hg(II) on stripping voltammetric determination of methylmercury was proposed. Its relay on complexation of Hg(II) by DTPA (ref.[1]).

In this communication a new procedure for methylmercury determination was described. In this procedure to increase the selectivity of methylmercury determination a gold film electrode coated with Nafion and complexation of Hg(II) by DTPA we exploited. To obtain low detection limit for methylmercury optimization of experimental parameters of electrode preparation and deposition of methylmercury was performed. Gold film electrode was prepared by electrodeposition of gold on glassy carbon from solution containing 6×10^{-4} M $AuCl_3$ + 0.025 M HCl + 4 g L^{-1} urea. The gold film electrode was then covered by Nafion film using pneumatic nebulizer from AAS apparatus. For this purpose 0.5% solution of Nafion in buthyl alcohol was used. The electrochemical procedure of electrode regeneration after the measurement was proposed.

In the course of optimization of conditions of methylmercury deposition following parameters were studied: pH of supporting electrolyte, concentration of DTPA, accumulation time and influence of Hg(II) concentration on methylmercury peak current. At optimized conditions methylmercury was determined in the range from 1×10^{-8} to 5×10^{-7} M in the presence of 2.5×10^{-5} M Hg(II). Interference of chlorides and nitrates on analytical signal of methylmercury was studied because HCl and HNO_3 are often used to extract methylmercury from solid samples.

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PP-18

DETERMINATION OF NICKEL BY ADSORPTIVE STRIPPING VOLTAMMETRY AT AN *IN SITU* PLATED BISMUTH FILM ELECTRODE

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Adsorptive stripping voltammetry has been established as a reliable trace metal analysis in cases, where the analyte forms intermetallic compounds or cannot form an amalgam, as *e. g.* Ni, Co or Cr. Procedures for these ions determination relay on interfacial accumulation of complexes of the target metals onto the working electrode and then reduction of the accumulated complex. In the case of Ni(II) determination, complexes with dimethylglyoxime or nioxime were most commonly exploited. Although reports on Ni(II) or Ni(II) and Co(II) determination at a bismuth film electrode can be found in the literature in all reported procedures, the electrodes were plated *ex situ*.

In this communication we present the procedure for Ni (II) determination by adsorptive stripping voltammetry in the presence of nioxime at *in situ* plated bismuth film electrode. For stabilization of Bi(III) added to the sample solution tartrate was introduced to the supporting electrolyte. It must be noted that Bi(III) should be added to the solution as its complex with tartrate to avoid its hydrolysis at mild alkaline conditions.

Taking into account the fact that in the proposed procedure for the first time the bismuth film electrode is plated *in situ* from a mild alkaline solution, to pH of 10, the optimization of conditions of plating bismuth film and Ni(II) determination was performed. At optimized conditions the calibration graph for the accumulation time of 120 s was linear from 5×10^{-9} to 5×10^{-8} M.

Two ways of regeneration of the electrode after measurements were studied and it was found that the best way of regeneration leading to reproducible results relay on reduction of accumulated metal ions to metallic state at –1.1 V.

Possible interferences by metal ions and surfactants were studied. The proposed procedure was validated by analysis of water certified reference material.

PP-19

PROPERTIES OF ION-SELECTIVE ELECTRODES WITH POLYMERIC MEMBRANES FOR KETOPROFEN DETERMINATION

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Ketoprofen, 3-benzoyl-α-methylbenzeneacetic acid is used in medicine as an analgesic and anti-inflammatory drug[1]. So far a number of methods of quantitative determination of ketoprofen have been applied, but they are relatively complicated, expensive and require a time-consuming preparation of a sample to analysis. Therefore, new methods are being developed, including potentiometric methods with ion selective electrodes used.

The aim of the research was to create the electrodes based on PVC membrane which are indirect contact with an Ag/AgCl electrode. The electrodes have not any inner solution and they posses all the advantages of the "coated wire electerodes". The detailed construction of the electrode was described in earlier paper[2]. The membranes were plasticized with bis(2-ethylheksyl)sebacate, dibutyl phthalate, diizobutyl phthalate, tris(2-ethylheksyl) phosphate, 2-nitrophenyloctyl ether in which the active substance tetraoctylammonium 3-benzoyl-α-methylbenzeneacetate was dissolved.

The basic analytical parameters of the ketoprofen electrode like: measuring range, detection limit, response time, life time, and selectivity coefficients for some organic and inorganic anions were determined. The electrode was used to determine ketoprofen in sinthetic sample and pharmaceutical preparations in injections, tablets and capsules. The examined electrodes can be applied to ketoprofen determination in the concentration range of 25–25 000 $\mu g\ mL^{-1}$ in water solution at pH 5.5–8.5. The statistical parameters (recovery 99–102 %, RSD < 3 %) indicate the typical accuracy of the analytical methods employing ion-selective electrodes.

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PP-20

ELECTROCHEMISTRY OR AAS FOR TRACE ANALYSIS OF METALS

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Trace concentrations of metals are usually determined by atomic spektrometry, mostly by graphite furnace atomic absorption spectrometry (GF AAS) and mass spectrometry with inductively coupled plasma ionisation (ICP MS). The superior selectivity, sensitivity and broad availability of the AAS method makes it usually the choice No 1 when seeking for a method for trace concentrations. Electrochemical methods also facilitate trace analysis of metals but cannot compete spectrometric methods owing to lower selectivity, limited number of metals measured, laborious and tedious procedures. Yet, in some cases electrochemical methods may reasonably complement or even exceed AAS:

1. analysis of samples with high salt contents for easily evaporating elements such as Hg, Cd, Pb, *etc.*,
2. determination of some semimetals such as As, Se, Sb,
3. speciation analysis, *e.g.* As(III)/As(V), Cr(III)/Cr(VI),
4. on-line process analysis where atomic spectrometers could hardly be employed.

Moreover, electrochemical sample pre-treatment can significantly improve the performance of AAS in special instances:

1. hydride forming elements can electrochemically be converted to the corresponding hydrides and measured by AAS,
2. metals and semimetals can be electroehemically preconcentrated on large surface electrodes and on stripping measured by GF AAS. In such a way matrix effects can be minimised and detection limits improved.

The purposes of the methods for metal preconcentration are often different, depending on whether the methods are applied in environmental or another field. The respective method needs to be efficient, give high sensitivity and selectivity, which is useful when used in combination with atomic spectrometry techniques. Preconcentration procedures are considerable tools in analytical processes, since their applications guarantee trace metal analyses in complex matrices and improve the performance of the analytical techniques. Moreover, the preconcentration procedures exploiting the clean chemistry concept and the reduction of samples/reagents consumption are extensively used. In this contribution the brief descriptions of the methods for preconcentration procedures related to electrochemical deposition are discussed, as well as some applications are presented.

This work was supported by the Slovak Grant Agency VEGA (project No. 1/0500/08) and APVV (project No. 0057-06).

PP-21

QSER OF 1-ARYL-5-BENZYLSULPHANYL-TETRAZOLES AND THEIR ELECTROOXIDATION AS A METABOLIC MODEL

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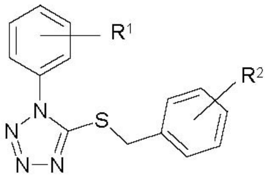
It is known, that the methods of quantitative structure-property and structure-activity relationships (QSPR/QSAR) are widely employed in the development of new pharmaceuticals. Recently, the term "quantitative structure-electrochemistry relationships" (QSER) has been adopted in the case of QSPR where the electrochemical properties (*e. g.,* half-wave potential, energy of HOMO) are correlated[1]. Electrochemical methods are useful tools not only for investigation of electron-transfer reactions but they can provide valuable information that helps understand some of the biological reactions, *e. g.* drug biotransformation[2].

One of the significant directions of current pharmaceutical chemistry is the search for new antimycobacterially active compounds. Proceeding in our previous study[3], we synthesized a new group of promising agents: 1-phenyl-5-benzylsulphanyltetrazoles.

In the first part of this paper, QSER of nineteen benzylsulfanyltetrazoles are reported. The second part of the work is concerned on preparative electrolysis and identification of oxidation products as a model for metabolic oxidation of studied compounds.



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PP-22

APPLICATION OF THE AMORPHIC TiO_2 IN VOLTAMMETRIC ANALYSIS

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Absorption of surface active substances (SAS) on a working electrode in voltamperometric techniques causes decrease or even diminishing of the analytic signal. Therefore, while using natural samples, specific pretreatment procedures are required.

One of the methods eliminating SAS-related influence on the measurement consists in addition of the fumed silica directly to the electrochemical cell[1,2].

In this paper it is suggested to replace fumed silica with titanium dioxide.

In an experiment the following chemical compounds were used: two forms of titanium dioxide (crystallic – anatase and amorphic – technically known as P-25 Degussa®), dodecylobenzenesulfonic acid sodium salt, hexaecyltrimetylammonium bromide and humic acids (Fluka Chemie GmbH) as SAS. SAS sorption on the titanium dioxide was estimated by a differential double-layer volume technique and a stripping-voltammetry.

As a result it was proven that:

1. Titanium dioxide added directly into the measuring cell in its' amorphic form of P25 (50 mg/10 mL) is much more effective in removing of humic acids, than crystallic form of titanium dioxide.
2. Sonification in the presence of P25 improves its effectiveness as humic acid sorbent (sonification without P25 is not so efficient).
3. Application of UV radiation increases P 25 sorption effectiveness and enables elimination of higher humic acids concentrations (up to 20 ppm).
4. In the presence of humic acids the addition of P25 improves depolarizer signal in voltammetric analysis.
5. Addition of 50 mg of P25 directly to the voltammetric cell causes decrease of depolarizer analytic signal by 3%, what suggests its sorption on titanium dioxide.

The study was financed by the Polish Ministry of Science and Education No. 18.18.160.579.

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PP-23

KAOLIN ROCKS AS ADSORBENT OF THE NON-IONIC SURFACTANT

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Certain amount of samples analyzed by means of voltammery is contaminated with the surface active substances (SAS). It induces application of the sample pre-treatment procedures. In the former papers, application of fumed silica as SAS adsorbent was described[1,2]. Herein, the use of some natural minerals – kaolin Osmoza, kaolin Imperial and kaolin Le Extra – as non-ionic SAS Triton X100 (TRT X100) adsorbents was examined. The results were related to the sorptive properties of fumed silica and cadmium ions were used to indicate sorption efficiency of the listed above adsorbents. From 80 mg to 500 mg of minerals per 10 mL of solution were added directly into the electrochemical cell. The stripping voltammetry technique was used for Cd concentration measurements.

It was found that:

1. The highest sorption efficiency of non-ionic SAS exhibited kaolin Osmoza.
2. At the same instant, depolarizer was most effectively adsorbed from the solution with 400 mg of kaolin Osmoza added.
3. Kaolin Osmoza may be used for the removal of non-ionic SAS up to its concentration of 2.5 ppm. Addition of 80 mg of kaolin to 10 mL of solution is needed.
4. The examined kaolin minerals were not selective, *i.e.* they adsorbed both – SAS and depolarizer ions.
5. Kaolin Le Extra was of no analytical use.

The study was supported by Ministry of Education and Science (AGH University Project No.11.11.160.799).

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PP-24

ADSORPTION OF METHIONINE AT A MERCURY/ AQUEOUS SOLUTION OF NaClO$_4$ INTERFACE; DEPENDENCE ON THE SUPPORTING ELECTROLYTE CONCENTRATION

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Methionine is an essential α-amino acid containing sulphur. It is indispensable to the correct functioning of organisms. Methionine has found a wide use in medicine for its detoxication, anti-inflammatory and antidepressant applications. It also enhances the pharmacological performance of lithium, antibiotics and sulfamides. Apart from that it has also been found a Bi(III) ions electroreduction catalizer[1]. Methionine adsorption on the mercury/chlorate(VII) interface was examined in 0.5 M to 8 M chlorate(VII) solutions. The course of the differencial capacity curves on mercury (Cd) in 0.5 M to 8 M chlorate(VII) solutions containing $0.5–50\times10^{-3}$ M methionine indicate a methionine adsorption on mercury/ chlorat(VII) interface. With the increase of methionine concentration the hump appearing on the $C_d = f(E)$ curves decreases and shifts towards the negative potentials. The same effect is observed with the increase of chlorate(VII) concentration in non-methionine containing solutions. The linear dependencies the potential of zero charge from methionine concentration obtained for all the examined chlorate(VII) concentrations point to a specific methionine adsorption on mercury electrode. Methionine relative surface excesses (Γ') were determined at constant electrode charge[2]. The surface excess values increase with increasing methionine concentration and electrode charge. The surface excess depends on the supporting electrolyte concentration. Along with the chlorates (VII) concentration increase from 0.5 M to 3 M methionine surface excess values rise in the electrode charge range from -8×10^{-2} C m^{-2} to $+13\times10^{-2}$ C m^{-2}. In 4 M and 5 M chlorates (VII) a considerable value decrease appears in methionine surface excess. A further base electrolytes concentration increase causes a slight surface excess value rise. The highest surface excess values were obtained in 3 M chlorates(VII). In methionine adsorption description the following isotherms were used: Frumkin, Viral, modified Flory-Huggins isotherm. Energy adsorption and constant interactions between the already adsorbed methionine molecules were appointed. The adsorption parameters change in the base electrolytes function point to a competitive methionine molecules and ClO_4^- ions adsorption as well as to a electrostatic interaction between methionine and water molecules.

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PP-25

ELIMINATION VOLTAMMOGRAMS OF MINIATURIZED MERCURY DROP ELECTRODES

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Elimination voltammetry with linear scan[1–4] in connection with renewed stationary mercury electrodes (HMDE/SMDE) can provide valuable information about nature and kinetics of processes at electrode interfaces. Its application is based on the unique treatment of voltammetric current-potential dependences measured at certain scan rates. In common cases the size of the HMDE does not change. Recent development of miniaturized mercury electrodes (MME) has brought much broader range of their accessible geometrical parameters[5–9]. Preliminary DC-voltammetric measurements using MME revealed the effect of its size on the shape and course of the measured peaks.

The aim of this study was to measure DC-voltammograms under controlled conditions using stationary mini- or semimicro-drop electrodes with different diameters and to apply corresponding elimination procedures. Procedures of preparation of the mentioned types of sensors were described. As it was expected, the course and parameters of the obtained elimination voltammograms depended on the size of the miniaturized renewed stationary mercury drop electrodes.

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P-26

RECENT PROMISING MINIATURIZED RENEWED MERCURY OR RELATED ELECTRODES AND PLASTIC SENSORS

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Renewed mercury and related electrodes still maintain[1–8] nowadays, almost 90 years after the discovery of polarography and 50 years after the award of Nobel prize to professor Jaroslav Heyrovský, their irreplaceable importance in physico-chemical, electrochemical and electroanalytical research and in the therewith connected wide practice.

Recently[2–8] new types of mercury, amalgam and composite amalgam sensors or analogously arranged sensors based on various other materials (of adequate rheological behaviour – liquids, pastes, mixtures, composites, gels, inks, solids) have been designed. For example[3–7], the attention has been paid to miniaturization as to their size or amount of active phase from mini-, semimicro-, micro- to nanolitre scale (mS, sμS, μS to nLS/nVS-sensors or elodes mE, sμE, μE, nLE/nVE); to capillary or plastic-tip sensors/elodes (PTS/E); to renewable forms [drops (DE), meniscus (ME) or hemisphere (HE)] and modes like DME, HMDE, SMDE, SMME, HMHE, ... elodes or DE, sME, or sHE incl. their staircase increasing/decreasing size, contraction/expansion, *etc.*; to their various materials (organic, inorganic, bio-), various arrangements of sensors, systems, pulse generators producing proper sequence of pulses, satellite control or monitoring, *etc.*

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PP-27

EFFECTS OF ELECTROLYTES ON THE NOISE IN THE OVER-LIMITING CURRENT RANGE

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This research work investigates the *i-v* and *V-t* curves, particularly the effect of the counter ion nature on the noise in the over-limiting current I_{ov}. The overlimiting current is always accompanied by a neat electrical noise. It is a well accepted experimental phenomenon[1–5] .The study of this may contribute to a better understanding of the I_{ov} nature and the water dissociation mechanism.

This research work presents original finding: The electrical noise depends directly on the counter ion nature. The noise intensity decreases according to the Hoffmeister series: $Li^+ > Na^+ > K^+$. We explain this by the hydratation number of the counter-ion. The ion NH_4^+ presents a singular behavior; the noise is minimal.

We are most grateful to Prof. Benachour Djaffer (Algeria), Prof. Tahar Bendaikha (Algeria), Prof. Saidani Boualam (Algeria), Prof. C. Gavach (France), Dr. F. Lutin (EURODIA, France), Prof. J. Benavente (Spain), Prof. Seung Hyeon Moon (Korea), Prof. Hubert Giraut (Lausanna), Dr. Maarten Van Brussel (The Netherlands).

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PP-28

THE CHEMICAL INVESTIGATING METHODS OF CONCENTRATION POLARIZATION IN ELECTRODIALYSIS

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This research work investigates the *i-v* and *v-t* curves, particularly the physical meaning of the plateau length of the limiting current I_{lim} and the nature of the over-limiting current (I_{ov}). In recent papers[1] Wessling *et al.* presented I_{ov} as a puzzle and a non elucidated problem. They concluded that electro-convection, theory proposed by Rubinstein, explains I_{ov}. Our research team has developed original experimental methods to investigate the *i-v* curve and related problems:

i) The buffer solutions method[2]: $HPO_4^{2-}/H_2PO_4^-$ used as co-ions or counter-ions[3,4].
ii) The weak electrolytes method[3,4]: the addition of phenol, boric acid.

We consider that these experimental results constitute clear and strong contributions to the *i-v* curve understanding and cannot be explained by electro-convection. Today we confirm this approach by new experiments which combine both properties: the buffer is NH_4^+/NH_3 and the neutral weak electrolyte is NH_3 Our experiments have been obtained automatically (AutolabPGSTAT30) and manually with classical membranes (CMV, CMX) and a free convection four electrodes cell.

We explain these results by the change of the dielectric properties of the membrane inside. Under the effect of very high local electric field (space charges), the pK_a of weak electrolytes is lowered (Wien effect and Booth equation) which improves the membrane conductivity. These phenomena explain I_{ov}. Our discussion will be based on the effects of weak electrolyte pK_a values and concentrations. The research works of Pintauro *et al.*[5] and Tanioka[6] constitute a strong literature confirmation of our new chemical experimental approach.

We are most grateful to Prof. C. Gavach (France), Dr. F. Lutin (France), Prof. Seung Hyeon Moon (Korea).

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PP-29

MODELLING OF WATER TRANSPORT IN A PROTON EXCHANGE MEMBRANE FOR FUEL CELL (PEMFC) EFFECTS OF POROSITY

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A model of water transport in a membrane electrode assembly (MEA) of a proton exchange membrane fuel cell is developed. The model takes into account, diffusion, migration, convection, and drags in the membrane phase and considers the membrane as a proton structure a porous structure. The mathematical model is solved using finite element tool. In this paper we had calculated and discussed one dimensional distribution of water in the cell with and without porosity.

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PP-30
ELECTROCHEMICAL SENSORS FOR HYDROPEROXIDES IN WATER AND ACETONITRILE

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Electrochemical catalytic effects can be a valuable analytical tool for determination and detection of many analytes. We have found that in water during electroreduction of Fe(III) in the presence of HOOH and *t*-BuOOH, cathodic catalytic currents could be registered, whereas in acetonitrile electrooxidation of Fe(II) in the presence of mentioned hydroperoxides gave anodic catalytic currents (where hydroperoxides acted as reducing agents)[1].

In present research cyclic voltammetry was used to investigate the electrochemical properties of modified GCE electrodes. The possibilities of obtaining the sensors for *t*-BuOOH and HOOH determination, working on the basis of electrochemical catalytic currents were considered. Immobilization of the catalyst onto the surface of the electrodes prevents contamination of the analytical sample. The electrodes under study were GCE modified with the Nafion doped with Fe(III) and GCE, modified with polyaniline, poly(*N*-methylaniline) and poly(*N*,*N*-diethylaniline), doped with Fe(II).

GCE/Nafion, Fe(III), electrode were proved to be useful for construction of disposable, sensitive sensors for HOOH and *t*-BuOOH in water. GCE/poly(*N*,*N*-diethylaniline), Fe(II); GCE/polyaniline, Fe(II); GCE/poly(*N*-methylaniline), Fe(II) electrodes can be used for construction of stable, reusable sensors for determination of HOOH and *t*-BuOOH in acetonitrile.

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PP-31
THE CORRELATION OF SODIUM, POTASSIUM, CALCIUM AND MAGNESIUM IONS IN HUMAN ORGANISM STUDIED BY POTENTIOMETRIC AND SPECTROFOTOMETRIC METHODS

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Magnesium as well as a number of other monovalent and divalent bioelements like sodium, calcium plays an important role in a proper work of whole chain of intracellular metabolism[1,2].

The aim of this job was determination of current contents of some bioelements (potassium, sodium, calcium and magnesium) in blood of randomly chosen age population *i.e.* 9th to 75th year of life and their statistic interpretation in relation to common interrelation.

A content of elements was determined using the method of spectofotometric and potentiometric. The values of obtained concentration of the determined bioelements have been drowning up according to the applied division into two groups (male and female). The obtained results were subjected to statistic analysis.

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PP-32
POTENTIAL-TIME RESPONSE OF BIOMIMETIC MEMBRANES IN PRESENCE OF ZINC AND MAGNESIUM IONS

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It was recently shown that the conducting polymer (CP) films doped with biologically active ligands may be used as model biological membranes to study the mechanism of membrane potential formation[1]. In particular the CP films may be used to study competitive binding of cations to biologically active ligands such as adenosine triphosphate (ATP) and resulting impact on transient membrane potential during equilibration.

In this study the interaction of magnesium/zinc ions with ATP was in focus. ATP is the universal energy currency for all known life forms. ATP and its reaction products provide or store energy for all organism activity. All the enzymatic reactions of ATP require the presence of metal ions able to interact with the nucleotide to form complex molecules that act as the real substrate. ATP-Mg species often accomplish this role, however other cations such as Zn(II), Cu(II), Mn(II) and Al(III) are of much importance for the biochemistry of ATP, and for toxicity effects related to interference in ATP-associated reactions[2,3].

The ATP ions were introduced into poly(pyrrole) and poly(3,4-ethylenedioxythiophene) films during electropolymerization. The CP films were conditioned to allow for the admission of Zn^{2+} or Mg^{2+}. The films sensitive for Zn or Mg ions were used as model membranes in potentiometric measurements. Close-to-Nernstian sensitivity was observed for the films under equilibrium. During equilibration, provoked by the change in concentration of Zn^{2+} or Mg^{2+}, a characteristic, and distinctively different for Zn and Mg ions, transitory potential response was observed. This behaviour is ascribed to the surface concentration changes of Zn and Mg due to the competitive binding at the ATP membrane sites during equilibration.

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PP-33

ARRANGEMENTS OF PLATINUM ELECTRODES IN AMPEROMETRIC DETECTORS FOR DETECTION OF HYDROXY AND AMINO DERIVATIVES OF POLYCYCLIC AROMATIC HYDROCARBONS

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The development of amperometric detection in liquid flow methods represents one of the most active and successful movements in electroanalytical chemistry. Among variety of materials used, platinum indicator electrodes remain popular due to their sensitivity, mechanical robustness, easy of electrochemical pretreatment and geometry variability[1].

This study compares two arrangements of platinum indicator electrode in home-made amperometric detectors. They consist from the pen-type reference and auxiliary electrodes placed in an overflow vessel close to Teflon tubing (1/16" o.d., 0.010" i.d.) joined to the column outlet. This tubing accommodates the Pt indicator electrode: The platinum tubular electrode (effective area 0.6 mm^2; ref.[2]) or the platinum microcylindrical electrode (geometric area 0.08 mm^2) made by fixing of a thin platinum wire in the Teflon tubing across to the flow of mobile phase.

Both detectors were employed for the detection of selected hydroxy and aminoderivatives of polycyclic aromatic hydrocarbons (naphthalenes, biphenyls) after their HPLC separation using reversed C_{18} phase and phosphate buffer – acetonitrile mobile phase. The Pt tubular detector is more sensitive with detection limits typically in the 10^{-8} M concentration range, while the Pt microcylindrical detector (detection limits typically in the 10^{-7} M concentration range) has the advantage of lower peak tailing, which would be covetable for analysis of more complicated mixtures. The reproducibility of the detector response is satisfactory in both cases even for aminonaphthalenes that are known to form polymerizing films as products of oxidation at platinum or carbon electrodes leading to electrode fouling.

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PP-34

COPPER AMALGAM ELECTRODES IN THE DETERMINATION OF ARSENIC, SELENIUM AND ELEMENTAL SULFUR

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The most of arsenic forms and compounds are very toxic and cancerogenic. Arsenic toxicity depends on its speciation *i. e.* compounds of As(III) are much more toxic than compounds of As(V). Considering the very low concentration limits of arsenic acceptable in the environment, drinking water, food and similar products[1]. Selenium is an important element in biological and environmental systems. Selenium is an essential trace element in human body. A lack or excess of selenium leads to several disease. In case of selenium gap between toxic concentration and concentration as bioelement is very narrow[2]. Thus a sensitive method of determining selenium and arsenic are necessary.

Elemental sulfur, S(0) is formed during the biotic and abiotic oxidation of dissolved sulfide and solid metal monosulfides. The data available on their amounts in marine pore waters are limited, and there is practically no data for pore waters of freshwater systems[3]. This lack of data is the result of a paucity of reliable analytical methods that could be used to determine low concentrations of elemental sulfur.

In the work the determination of trace arsenic, selenium and elemental sulfur were carried out using differential pulse cathodic stripping voltammetry (DPCSV) at the copper amalgam electrodes. The proposed method is easily optimized. The detection limit for As(III) as low as 25 ng L^{-1} (preconcentration time (240 s) for Se(IV) as low as 20 ng L^{-1} (preconcentration time 120 s) and for S(0) as low as 14 ng L^{-1} (preconcentration time 60 s) could be obtained.

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PP-35

APPLICATION OF THE ELECTRODE TYPE Hg(Ag)FE IN THE DETRMINATION OF MOLYBDENUM, MANGANESE AND SELENIUM

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Most voltammetric methods required mercury electrodes. The Hanging Mercury Drop Electrode (HMDE) is the electrode of preference due to its high sensitivity, reproducibility and linearity. However, the toxicity of mercury limits the usage of the mercury electrodes in the analytical practice and excludes them from the out-of-laboratory applications. The problem of limiting the amount of mercury or its soluble salts needed for the analytical procedure can be solved with the help of a Renewable Silver Amalgam Film Electrode (Hg(Ag)FE). The principle of working and first proposal of a Hg(Ag)FE electrode construction was made by Baś and Kowalski[1]. The construction the cyclic renewable mercury film electrode is depicted on Fig. 1.

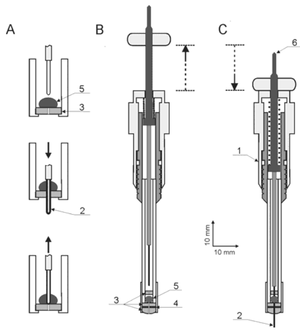

Fig. 1. **The principle of mechanical refreshing of the mercury film silver based electrode.** The Hg(Ag)FE used in our experiments: (1) micrometric screw, (2) piston pin with Ag cylindrical electrode at the end, (3) O-ring, (4) Ag foil (0.05 mm), (5) liquid Ag amalgam (~10 µl), (6) electric contact pin

The Hg(Ag)FE refreshed before each measurement demonstrates many properties which are specific only to the hanging mercury electrode[2–4]. The preparation of the Hg(Ag)FE is very simple and regeneration of the mercury film is easy and very short. The Hg(Ag)FE was successfully applied for the determination of Mo, Mn and Se.

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PP-36

ELECTROCHEMICAL DETERMINATION OF DICLOFENAC SODIUM IN AQUEOUS SOLUTION ON Cu-DOPED ZEOLITE – EXPANDED GRAPHITE-EPOXY ELECTRODE

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Diclofenac is a common anti-inflammatory drug. In recent years, pharmaceutical drugs constitute a novel class of water contaminants[1–4], and their determination by a fast and simple method is necessary.

An electrochemical sensor based on Cu-doped zeolite-modified expanded graphite-epoxy composite electrode was evaluated for a new alternative of quantitative determination of sodium diclofenac in aqueous solutions. Cyclic voltammetry was used to characterize the electrochemical behaviour of the electrode in the presence of sodium diclofenac in 0.1 M Na_2SO_4 and 0.1 M NaOH supporting electrolyte. This modified electrode exhibited electrocatalytic effect towards sodium diclofenal oxidation, allowing its determination in aqueous solution. The linear dependence of the current versus diclofenac concentration was reached using cyclic voltammetry, differential-pulsed voltammetry, and chronoamperometry.

Substantial enhancement of electrode sensitivity for the determination of sodium diclofenac at Cu-doped zeolite-modified expanded graphite-epoxy composite electrode was reached by applying a chemical preconcentration step prior to voltammetric quantification. Also, under these last conditions better the lowest limit of detection was achieved, allowing the analytical utility of this electrode over a concentration range where aquatic sodium diclofenac pollution is known to occur.

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PP-37

ELUCIDATION OF ELECTRODE REACTION MECHANISMS BY DIFFERENTIAL PULSE POLAROGRAPHY

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The use of computers in the control of the experiments was a key factor for the rebirth of polarographic techniques in the 90's decade. From the discovery of d.c. polarography by J. Heyrovsky, other techniques were developed such as tast, normal pulse, NP, differential pulse, DPP, or a.c. polarography. DPP is a widely used electroanalytical technique because the decrease in the charging current's relative contribution of the measured current. The DPP parameters that can be changed are the pulse amplitude and the pulse duration. The selectivity and sensibility of the technique can be increased by controlling both parameters. But DPP can be also used in electrode kinetics, and the aim of this communication is to show its utility in this task.

Though equations obtained from rigorous theoretical treatments are difficult to handle to obtain kinetic parameters, approximate equations were developed, allowing the kinetic analysis[1–7]. By exploring the different parameters of the technique, DPP can be used for the elucidation of the kinetics of the electrochemical processes (with the evident exception of the product and intermediate identification). So, the type of transport (diffusional or chemical) can be evidenced from the dependence of the currents with the pulse amplitude[4], the electrochemical reaction order with respect the electroactive species from the shape of the polarogram[1,2,5], the type of rate-determining step from the dependence of the peak potentials on the pulse duration[4], the electrochemical reaction order with respect other species, such as the H^+ ion, from the dependence of the peak potentials on their concentrations[1,2,4,5,7] *etc.*

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PP-38

ELECTROCHEMICAL CATALYTIC CURRENTS FORMED IN THE PRESENCE OF DIOXYGEN AND TRANSITION METAL COMPLEXES OF SALEN

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The mechanism of activation of dioxygen by means of transition metal complexes is very important in many aspects of chemical study as well as biological transformations. In these processes the intermediates with incorporated oxygen are formed[1–3]. They can be a source of oxygen in the reaction of oxidation of organic compounds, and can substitute classical oxidants *i. e.* heavy metal salts. Understanding of dioxygen activation mechanism will lead to development in many fields connected with „Green Chemistry", waste products management, and biochemical reactions occurring in living organisms[4,5].

Recently we have found that in acetonitrile, $[Fe^{II}(salen)]_{solv}$ is rapidly oxidized by dioxygen to give Fe(III) complex. The exposition of the solution to air or dioxygen atmosphere causes the complete oxidation of $[Fe^{II}(salen)]_{solv}$. Electrochemical reduction of $[Fe^{III}(salen)]^{+}_{solv}$ formed, causes the increase of observed current, which indicates that the catalytic process occurs and reactive oxygen species are formed during that processes. It is very interesting that the observed increase of the catalytic current is the same in the presence of dioxygen and air. We also tried to employ preparative electrochemical reduction of system containing $[Fe^{III}(salen)]^{+}_{solv}$ and dioxygen to oxidation of unsaturated hydrocarbons. This attempts were unsuccessful due to the deactivation of electrode surface by decomposed complex. However, we have found that metal-salen complexes activate dioxygen for oxidation of unsaturated hydrocarbons.

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PP-39

Zn^{2+} ELECTROREDUCTION MECHANISM AT MERCURY INTERFACE/CONCENTRATED $NaClO_4$ SOLUTIONS IN THE PRESENCE OF TETRAMETHYLTHIOUREA

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Based on the literature[1] we know that the increase of $NaClO_4$ concentration from 0.2 M to 7.0 M causes an increase of the true standard rate constants, k_f^t for Zn^{2+} ions reduction, but only for $NaClO_4$ concentration ≥ 1.0 M. We showed[2] that the catalytic activity of tetramethylthiourea (TMTU) decreased in the order 1.0 M $NaClO_4$ > 0.5 M $NaClO_4$ > 0.1 M $NaClO_4$.The studies on adsorption and catalytic activity were carried out in $NaClO_4$ solutions of the following concentrations: 2 M, 3 M and 4 M. The relative surface excess values of TMTU increased with the increase of $NaClO_4$ concentration. The obtained k_f^t values for Zn^{2+} ions reduction in the presence of TMTU in 2 M, 3 M and 4 M $NaClO_4$ were distinctly higher than for diluted solutions. In diluted $NaClO_4$ solutions a distinct acceleration effect rise appeared in the true standard rate constants values, which characterizes the first electron transfer stage and the second electron exchange stage[2]. In the currently studied systems, the second electron transfer stage maximum value rise, practically did not depend on the base electrolytes concentration. This may be the result of a similar Zn^{2+} aquaion composition.

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PP-40

ADSORPTION OF TETRAMETHYLTHIOUREA AT MERCURY ELECTRODE IN THE PRESENCE OF 1-DECANESULFONIC ACID

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The following study describes 1-decanesulfonic acids and tetramethylthiourea (TMTU) adsorption process at mercury electrode in 1 M $NaClO_4$. In this process the first substance adsorbs physically at mercury electrode whereas the second one undergoes chemisorption. After adding TMTU to the solution containing 7.5×10^{-4} M 1-decanesulfanic acid the following reactions were observed: an increase of differencial capacity, a distinct formation of TMTU desorption peaks, a significant surface tension decrease and a zero potential charge shift towards more negative potentials. The TMTU molecule occupied 0.152 nm^2 of the surface which was a considerably smaller amount than in the absence of the detergent. The A interaction constants obtained from Frumkin and Flory-Huggins isotherms point to a weak repulsive interactions between the TMTU molecules, which rise towards more negative electrode potentials. The $\Delta G°$ adsorption energy increases with the rise of electrode charge, however its adsorption energy increase is smaller compared to the ones in the absence of the detergent[1]. Inner layers electrostatic parameters were determined using Parsons' electrostatic model[2]. A dependence between all electrostatic parameters and electrode charges was proven.

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PP-41
ADSORPTION OF 1-DECANESULFONIC ACID AT MERCURY ELECTRODE IN 1M $NaClO_4$ SOLUTION

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1-Decanesulfonic acid is a biological detergent used to separate nucleic acids and proteins from their cellular structures. The adsorption studies were carried out below critical micellar point. The detergent concentration increase not only caused a distinct differential capacity and surface tension decrease but also a zero charge potential shift towards less negative potentials. The maximum adsorption[1] of 1-decanesulfonic acid appeared at –0.463 V potential and at $q = 0$ electrode charge. The adsorption parameters were determined using Frumkin and Flory-Huggins[2] adsorption isotherms in the electrode charges range from $-2\ \mu C\ cm^{-2}$ to $+2\ \mu C\ cm^{-2}$. The conducted studies found that for $q = 0$ the weakest repulsive interactions between 1-decanesulfonic acid ions occurred and that the free $\Delta G°$ adsorption energy reached its greatest value. The obtained adsorption parameters justify 1-decanesulfonic acid greatest value of surfaces excess for $q = 0$.

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PP-42
GLASSY CARBON ELECTRODES MODIFIED WITH PEDOT/PSS: OPTIMIZATION STUDIES FOR TRACE LEAD DETECTION

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The polyelectrolyte poly(sodium 4-styrenesulfonate), PSS has already been successfully used to coat a glassy carbon/thin mercury electrode (GC/TMFE) and applied to the square-wave anodic stripping voltammetry (SWASV) of trace metals[1,2]. However, it still needs an optimization in order to present the better relation between a high density of $-SO_3^-$ groups on the deposited coating and low leakage of this coating to the test solution, consequently broadening the voltammetric signal[2]. On the other hand, the conducting polymers are often fruitfully employed as redox-mediators towards several analytes, significantly enhancing sensitivity and selectivity of the analytical detection and even lowering the detection limit[3]. PEDOT is considered the most stable conducting polymer currently available, being especially attractive when high stability of the polymeric material is required[4].

PEDOT-PSS complex is the most widely utilized because it has a good shelf life, can be easily coated on various substrates to form thin films by many methods, thus showing good film-forming properties, and displays an excellent stability[5,6]. PEDOT-PSS composite films behave as a cation exchanger[7].

In the present study, the incorporation features of such PEDOT-PSS coatings towards lead(II) accumulation in the polymer film are optimized regarding some features like: scan rate used for the electropolymerization, number of scans, EDOT:PSS ratio present in the electropolymerization solution. The stability reproducibility and repeatability of the selected coating of PEDOT-PSS were also evaluated.

Thanks are due to "Fundação para a Ciência e Tecnologia" (FCT) for financial support (Project POCI/AMB/55939/2004).

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PP-43
KINETICS OF HETEROGENEOUS ELECTRON TRANSFER REACTIONS IN IONIC LIQUIDS

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Heterogeneous electron transfer rate constants, k_{het}, of organic molecules have been measured by cyclic voltammetry in three different room temperature ionic liquids (RTILs): $[emim][BF_4]$, $[bmim][PF_6]$ and $[bmim][CF_3SO_3]$. Various organic acceptor (A) and donor (D) systems:

$$A + e^- \xrightarrow{k_{het}} A^{\bullet -},\ D \xrightarrow{k_{het}} D^{\bullet -} + e^-$$

like ferrocene, chloranil, bromanil, methylviologen (MV), ethylviologen (EV), tetracyanoethylene (TCNE), *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPPD), tetrathiafulvalene (TTF) and *p*-phenylenediamine (PPD) are used. The

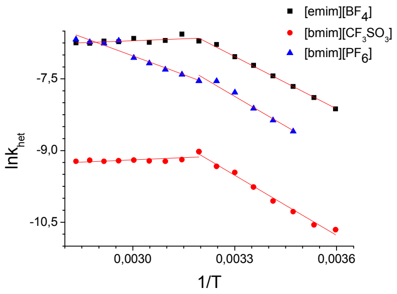

Fig. 1. **Fe(cp)$_2$ in three different RTILs**

results obtained in RTILs are compared with those found in organic solvents, like CH_3CN *etc.*[1]. Diffusion coefficients have been calculated in these ionic liquids and have also been compared with those found in classical organic solvents[2]. They depend on the inverse viscosity for all molecules under investigation. An interesting behavior has been observed in RTILs while plotting ln *D* against 1/*T*. This Arrhenius plot shows two different linear slopes with transient temperature of 313K (almost) for all three RTILs. Although few temperature studies in RTILs has been reported in literature but this two different slope trend has not been mentioned over there[3]. The same behavior was also observed when plotting ln k_{het} versus 1/*T* using Marcus equation. These two different linear slopes results in two different values of activation energy for the electron transfer. The main problem arising here to understand the role of λ_o which is describe by dielectric constant ε_S and a refractive index *n*. Such a concept is not applicable to the charged ions of the ionic liquids acting as solvents.

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PP-44

FASTER VOLTAMMETRIC ASSAY OF WATER SOLUBLE PHTHALATES IN BOTTLED AND COOLER WATERS

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Phthalic acid and phthalates esters are of growing interest due to their significant use and potential toxicity. A faster, simpler and highly sensitive Square Wave Voltammetric (SWV) method was developed for evaluation of total water soluble phthalates by taking 95% aqueous di-*n*-butyl phthalate (DBP) as a model at glassy carbon electrode. The study showed that 100 µM aqueous solution of DBP gives best response with 0.05 M tetrabutylammonium bromide, at stirring rate of 1400 rpm, deposition time, 20 s and pH 4.0. The optimum frequency and scan rate was 100 Hz and 0.9 V s^{-1} respectively. Voltammetric response was linear in 3 ranges, 70–110 µM, 20–60 µM and 2–10 µM with regression coefficient of 0.9873, 0.9978 and 0.9935 respectively and limit of detection 0.47 µM for total water soluble phthalates in aqueous medium. The developed method was successfully applied for total phthalates determination in various samples of water stored in PVC coolers and plastic bottles.

PP-45

AN IDEA FOR ION-SELECTIVE SENSOR: MODIFICATION OF THE GOLD ELECTRODE SURFACE BY CALIX[4]ARENE SELF-ASSEMBLED MONOLAYER

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The aim of this work is the use of molecules which belong in the large group of substances permitting transport of ions through biochemical membranes (ionophores) for development of an electrochemical, ion-selective sensor.

The modified, synthetized calixarene molecules, with four sulphur-containing groups located at the lower rim, were used as the ionophores. The calixarene molecules were covalently bonded to the surface of a gold disk electrode through the sulphur atoms. A self-assembled monolayer (SAM) was formed on the electrode surface, which altered the electrochemical properties of the electrode, compared to the bare electrode.

The preliminary results, obtained by the atomic force microscopy (AFM) measurements, indicate that the calixarene molecules form aggregates on the electrode surface, which have monodisperse size, and the calixarene SAM inhibits the gold electrode oxidation.

Electrochemical measurements by cyclic voltammetry permitted the calculation of a Langmuir-type adsorption isotherm for the formation of the calixarene SAM. Two modes of the calixarene adsorption process were compared, adsorption in the absence of any external electric potential applied to the gold electrode, and the electrochemical adsorption. It seems that calixarenes are more readily adsorbed from chloroform solutions, without applying any potential to the electrode. Electrochemical impedance spectroscopic measurements have demonstrated that the SAM-covered electrode has the impedance different from that of the bare electrode.

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PP-46

EVLS AS A NOVEL AND PROMISSING MATHEMATICAL APPROACH IN VOLTAMMETRIC METHODS

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Cyclic Voltammetry (CV) and Square Wave Voltammetry (SWV) belong to the most powerful electrochemical techniques that can be applied for both analytical and electrokinetic measurements at static drop or solid electrodes[1], because these methods, on one hand, are easy-to-use and low cost with fast scan rates and, on the other hand, have the ability to show the reversibility of redox reactions[2]. In addition, Elimination Voltammetry with Linear Scan (EVLS) belongs to the newest powerful electrochemical tools. This method provides an improvement of voltammetric results through eliminating and conserving various particular currents, of which the total recorded current is composed[3–5]. The elimination process provides further information on electrochemical mechanisms. In this study, the behavior of Cd(II), Zn(II) and Cu(II) in the presence of chloride ions (pH ranging from 3 to 9) at two electrodes, particularly, paraffin impregnated graphite electrode (PIGE) and hanging mercury drop electrode (HMDE), measured by CV and SWV was compared. The voltammetric data was further processed by EVLS. The values of elimination coefficients of elimination functions for different scan rate combinations were calculated by Matlab program.

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PP-47

THE DETERMINATION OF DIZEPAM, TEMAZEPAM AND OXAZEPAM AT THE LEAD FILM ELECTRODE BY ADSORPTIVE STRIPPING VOLTAMMETRY

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The determination of psychoactive 1,4-benzodiazepine drugs is of relevant interest in clinical, biomedical areas. The voltammetry methods seem to be efficient tools for a quantitative determination of 1,4-benzodiazepine drugs in pharmaceutical preparations and biological fluids in a simple and economic way. Therefore highly sensitive and simple voltammetric method for the determination of temazepam, diazepam and oxazepam at *in situ* plated lead film electrode was developed.

Till now the lead film electrode has been used for the determination of inorganic ions[1] such as Ni(II), Co(II), U(VI), Mo(VI) and organic compounds[2] such as folic acid, trimethoprim, testosterone, glipizide, rifampicine, rutin and sildenafil citrate (Viagra). Although lead compounds used for plating a lead film are toxic, their toxicity and volatility is lower as compared to the mercury and mercury compounds used for the preparation of mercury electrodes.

In this presentation it was shown that determination of 1,4-benzodiazepine drugs by adsorptive stripping voltammetry was possible using an *in situ* plated lead film electrode. The proposed procedures are based on temazepam, diazepam and oxazepam adsorption on the lead film electrode in the accumulation step and then the reduction of compounds during the stripping step.

The optimized procedures were applied to the determination of temazepam and diazepam in the presence of other components in pharmaceutical preparations with minimum sample manipulation. The analysis of diazepam and temazepam were performed much more rapidly than by previously reported voltammetric techniques. The procedure for determination of oxazepam was successfully used for determination of this compound in human urine samples directly without any separation steps.

The authors thank the Ministry of Science and Higher Education for financial support (project no. N204 1472 33).

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PP-48

ON LINE DIFFERENTIAL PULSE POLAROGRAPHIC DETERMINATION OF COBALT(II) AT PPB CONCENTRATIONS IN ZN PLANT ELECTROLYTE

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The purification process control of industrial $ZnSO_4$ solutions used for Zn electroextraction requires simple, rapid and reliable methods for trace (ppb) concentrations determination of: Cd^{2+}, Cu^{2+}, Pb^{2+}, Sb^{3+}, Co^{2+}, Ni^{2+}, Ge^{4+} in the presence of about 150 g L^{-1} $ZnSO_4$. The high Zn^{2+} concentration makes the application of the AAS and ICP complicated, long and less precise, requiring preliminary laboratory analyte separation.

The high ionic concentrations of the Zn plant electrolyte however favors the application of the voltammetric methods for the determination of almost all these impurities except Co^{2+} and Ni^{2+} defined by Bond as impossible[1] because of the complete peak overlapping with the huge peak of Zn^{2+}.

A simple and rapid Differential Pulse Polarographic (DPP) method with DME application for direct on line Co^{2+} determination in Zn plant electrolyte was developed and tested with real industrial solutions. The method is based on the Co^{2+} to Co^{3+} oxidation by 1-nitrozo-2-naphtol in pH 9 ammonia buffer used as supporting electrolyte in which the sample is added directly on line. The DPP Co^{3+} peak appear at –550 mV (SCE) and the great E½ potential difference completely eliminates the Zn^{2+} interference as shown in Fig. 1.

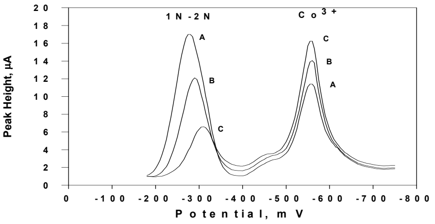

Fig. 1. **DPP curves of ammonia buffer with pH 9, containing 1-nitrozo-2-naphtol and Co^{2+} additions of: 4 ppb (curve A), 5 ppb (curve B) and 6 ppb (Curve C)**. $\Delta E = -50$ mV

Unlike the stripping method of Braynina[2] based on electrochemical deposition of 1-nitrozo-2-naphtol chelate of Co^{3+} layer on a graphite electrode followed by DC anodic dissolution, the proposed DPP determination is direct and rapid. The high precision of the results (4.2 % rel. at 20 ppb) and the wide linear concentration range covering entire range of Co^{2+} concentrations in Zn plant electrolyte (from 1 to about 500 ppb) make it suitable for on-line application.

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PP-49

IN SITU As(III) DETERMINATION IN THE PRESENCE OF Pb(II) BY DIFFERENTIAL ALTERNATIVE PULSES VOLTAMMETRY

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The Differential Alternative Pulses Voltammetry (DAPV) introduced by the author earlier[1] combines the high sensitivity of the Differential Pulse Polarography (DPP) and the high resolution power of the second order polarographic techniques. The small peaks half-width and the shape of the DAPV curve, as second derivative of the polarographic wave allow direct simultaneous determination of species having very small E½ difference as well as at high concentration ratios using the peaks situated at both side of the zero line (Figure 1).

DAPV was applied for direct determination of As(III) in ground water containing also Pb(II) using HCl as supporting electrolyte where the As(III)/Pb(II) E½ difference is about 40 mV. No chemical pretreatment procedure was applied for analyte separation. Complete peak overlapping occurs at 0.5:1 Pb(II) to As(III) concentration ratio applying DPP, while the DAPV application yields distinct peaks registration up to ratio as high as 12:1. The DAPV allows reliable, rapid, simple and

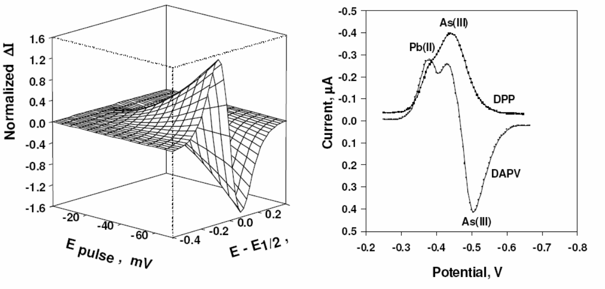

Fig. 1. **Theoretical DAPV curves (left); DPP and DAPV polarograms of Pb(II) and As(III) at 0.5:1 ratio in HCl (right)**

precise *in situ* As(III) determination preventing thus its oxidation to electrochemically inactive As(V) by the oxygen during the sample transportation to the analytical laboratory.

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PP-50

THE USE OF MERCURY MENISCUS MODIFIED SILVER SOLID AMALGAM ELECTRODE IN VOLTAMMETRIC ANALYSIS OF GENOTOXIC NITRO DERIVATIVES OF FLUORENE AND 9-FLUORENONE

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Nitro derivatives of polycyclic aromatic hydrocarbons (NPAHs) originate mainly from anthropogenic fossil fuel combustion and belong to the group of genotoxic compounds with proven negative biological effect on living organisms. That is why the need for extremely sensitive and selective methods of NPAHs determination is still growing[1]. Easy electrochemical reducibility of nitro group at aromatic rings enables successful use of electroanalytical methods for NPAHs determination[2]. Recently, great attention has been paid to electrochemical determination of nitro derivatives of fluorene and 9-fluorenone (namely 2-nitrofluorene, 2,7-dinitrofluorene, 2-nitro-9-fluorenone and 2,7-dinitro-9-fluorenone) at a hanging mercury drop electrode (HMDE) (ref.[2]). In this work, the main disadvantage of HMDE – low mechanical stability of mercury drop limiting the use of this electrode for field applications – has been eliminated by using the mechanically robust mercury meniscus modified silver solid amalgam electrode (m-AgSAE) (ref.[3]).

DC voltammetry (DCV) and differential pulse voltammetry (DPV) at m-AgSAE have been used for the determination of genotoxic fluorene derivatives mentioned above. Reached limits of quantification were around 10^{-6} M for DCV at m-AgSAE and M for DPV at m-AgSAE. Obtained results were compared with previous determinations of these substances at mercury electrodes[2]. The electrode mechanisms of tested substances at m-AgSAE have been also proposed and discussed.

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PP-51

EFFECT OF POLY(DIMETHYLDIALLYL-AMMONIUM CHLORIDE) ON ENZYME ENCAPSULATION INTO A SOL-GEL MATRIX

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Modification of sol-gel materials for development of organic-inorganic hybrid materials with additional properties or improved performance is a fast growing field for surface treatment technology[1], and (bio)sensing applications[2]. One convenient route to form a hybrid is the introduction of a polymer into the sol-gel matrix. This macromolecular compound can provide additional reactivity depending on the chemical functions hold by the polymer while the inorganic matrix induces good mechanical stability and suitable porosity. This kind of composite has been successfully used for electroanalysis when doped with poly(vinylsulfonic acid) or poly(dimethyldiallylammonium chloride) (PDMDAAC) (ref.[3]). The ion-exchange properties of the encapsulated polyelectrolyte allow using this sensor, for example, in Hanford tank waste simulant solution[4].

Silica sol-gel is considered as a favourable matrix for long time encapsulation of protein or even whole cells[5]. We are currently interested in the encapsulation of D-Sorbitol Dehydrogenase and Galactitol Dehydrogenase for applications in electroenzymatic synthesis. We observed that the direct encapsulation into a pure silica sol-gel matrix led to total suppression of enzyme activity, as characterized electrochemically. The lack of diffusion into the gel or the unfavourable electrostatic environment created by surface silanol groups could explain this inactivity. We will show here that the introduction of the suitable content of PDMDAAC into the sol during the bioencapsulation permits to maintain very good catalytic properties. This polyelectrolyte, in combination with sol-gel allows the elaboration of stable modified electrode. This is an important step for the development of electrochemical reactors based on immobilized enzymes.

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PP-52

PRUSSIAN BLUE BASED PLANAR BIOSENSOR FOR LACTATE DETERMINATION IN BLOOD AND SWEAT

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The construction of sensors is based on the approach for operation of oxidase based biosensors on electrodes modified by electrochemically deposited Prussian Blue (ferric hexacyanoferrate). The approach was first demonstrated by our team in 1994 (ref.[1]) and had been developed in order to achieve the most advantageous H_2O_2 transducer.

Electrochemical biosensor for lactate has been made by immobilization of the enzyme lactate oxidase on the top of planar sensor for hydrogen peroxide produced by Ltd Rusens. Immobilization protocol included a formation of the enzyme containing R-oxy siloxane membrane according to procedure developed earlier[2]. Exposure of lactate oxidase to water-organic mixtures with a high (90 %) content of the organic solvent, resulted in stabilization of the enzyme by membrane-forming polyelectrolyte. The corresponding biosensor has following analytical characteristics: improved sensitivity (about 70 mA M^{-1} cm^{-2}) and signal-to-noise ratio, low detection limit to compare with known analogs. Lactate may be analyzed in range from 1×10^{-6} M to 1×10^{-3} M in FIA regime.

During intensive sport training the concentration of lactate increases in 10–15 times in comparison with basic concentration. The dynamics of lactate concentration increasing allows to determine the most perspective athlete in such activities as boat racing, athletics, cross country skiing. The task was to develop the non-invasive methods of lactate determination. The most suitable biological liquid for such determination is sweat. In this research we used developed biosensors for determination lactate in blood and sweat as well as for estimation their correlation during sports training.

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PP-53

DETERMINATION OF 1-NITROPYRENE, 1-HYDROXYPYRENE AND 1-AMINOPYRENE IN HUMAN URINE BY HPLC WITH ELECTROCHEMICAL DETECTION BASED ON BORON DOPED DIAMOND FILM ELECTRODE

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Many polycyclic aromatic hydrocarbons (PAHs) and nitrated polycyclic aromatic hydrocarbons (NPAHs) are well known to be carcinogenic or co-carcinogenic compounds[1]. For example, 1-nitropyrene is one of the most abundant representatives of nitro aromatic compounds in the environment which has also been detected in automobile exhaust gas, urban air, exhalation from the incinerators, and in certain foodstuffs such as grilled meats or teas[2–4]. It is also listed in the IARC Monographs on the Evaluation of Carcinogenic Risks to Humans in the group 2B (possibly carcinogenic to humans).

A valuable tool in assessing human exposure to PAHs and NPAHs is the use of biological markers. 1-Nitropyrene (1-NP) and its urinary metabolites 1-aminopyrene (1-AP) and 1-hydroxypyrene (1-HP) have been proposed as biological markers for these purposes.

Most of analyses of PAHs and NPAHs in environmental samples are carried out by gas chromatography coupled with mass spectrometry, or by high performance liquid chromatography (HPLC) with fluorescence detector or UV/VIS detector. However, these methods are characterized by high investment and running costs. Because these analytes are easy electrochemically oxidizable and/or reducible, we have investigated the possibility of their determination by HPLC coupled with electrochemical detection based on boron doped diamond film electrode. We have found that this type of detection is sufficiently sensitive, selective and moreover it has much lower investment and running costs.

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PP-54

ENRICHMENT OF HYDRIODIC ACID USING ELECTRODIALYSIS CELL IN SULFUR IODINE PROCESS FOR HYDROGEN PRODUCTION

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The present work investigates the electrodialysis cell for concentrating hydriodic acid in thermochemical water-splitting sulfur iodine (SI) process for hydrogen production. The SI process consists of three coupled chemical reactions, such as the Bunsen reaction, the sulphuric acid decomposition reaction, and the HI decomposition reaction[1]. The hydriodic acid concentration part in HI decomposition section is the most energy consuming process because the HI_x solution ($HI–I_2–H_2O$ mixture) produced from the Bunsen reaction is present as an azeotropic mixture[2]. Therefore, the distillation part to concentrate the hydriodic acid requires considerable excess thermal energy, which can decrease the overall thermal efficiency of the SI process. Our research group reported that overall thermal efficiency is crucially influenced by both cell voltage and water transport of the electrodialysis cell[3]. In this work, the electrodialysis cell were prepared by consisting a polymer electrolyte membrane sandwiched between two carbon electrodes, gaskets, and carbon blocks with flow channels for distributing the reactant HI_x solution[4]. The cell voltage and water transport were measured with different operating conditions and their results were analyzed by combining theoretical calculations.

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PP-55

AN INVESTIGATION OF THE ELECTRO-CATALYST USED AS ELECTRODE MATERIALS IN SO_2-DEPOLARIZED ELECTROLYZER

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The SO_2-depolarized electrolyzer (SDE) used in the hybrid sulfur process oxidizes sulfur dioxide to form sulfuric acid at the anode[1] and reduces protons to form hydrogen at the cathode[2]. The important attribute of the SDE is the lowering of the electrode potential for producing hydrogen from 1.23 V *vs.* reversible hydrogen electrode (RHE), which is the equilibrium potential at standard state pure water electrolysis, to 0.158 V_{RHE} (ref.[3]). This means that SDE could more efficiently produce hydrogen with lower power as compared with pure water electrolysis. It was reported that 390 mV_{RHE} overpotential were generated at the anode and 50 mV_{RHE} at the cathode in the SDE, when 200 mA cm^{-2} of current density was applied during SO_2 oxidation reaction in a 50 wt.% H_2SO_4 solution. Therefore, it is necessary to reduce the anodic overpotential in order to improve the performance of the SDE. In the present work, the electro-catalyst utilization at anode was estimated using cyclic voltammograms (CVs) as a function of catalyst loading amount in a deaerated 4.8 wt.% H_2SO_4 solution. Then the CVs were measured on the electro-catalyst in SO_2-free and SO_2-saturated 50 wt.% H_2SO_4 solutions in order to confirm the mechanism of SO_2 oxidation reaction. Finally, linear sweep voltammograms were obtained with various loading amounts in order to determine the effect of loading amount on SO_2 oxidation reaction.

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PP-56

ELECTROCHEMICAL REMEDIATION. PAIRED RECOVERY OF A SOIL METAL POLLUTANT AND ITS EXTRACTANT, AT THE MICROSCALE LEVEL

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Soil are frequently the depositories of a wide range of wastes[1,2], atmospheric deposition can also contribute to soil pollution. Prevention strategies can undoubtedly ameliorate this problem; however, remediation technologies are of immediate emergency in many instances.

There is a wide variety of soil remediation based on physical, chemical, electrochemical or biochemical principles[35]. A modern alternative is metal complexation. It is based on the idea that metal complexes with chelating agents are frequently soluble and generally quite strong due to the chelate effect. Is it that, polluting metal ions is difficult to remove from chelate containing washing solutions by alkalinization, due to the intrinsic thermodinamic stabilities of the metal chelates.

The objective of this work was development an experiment in microscale to demonstrate the removal of a metal from an insoluble compound of $CuCO_3.Cu(OH)_2$ and EDTA by complexation followed by the simultaneous electrochemical recovery of the ligand (EDTA) and the metal (Cu) in its elemental form.

To recover both, the polluting metal and the extractant, an electrochemical process is worn. Using a micro electrochemical cell with a small U-tube, that containing the Cu-EDTA solution, and introduced a Pt wire into one arm of the tube as anode, and a graphite rod in the other arm as the cathode, at an applied potential of 10–11 V.

In this treatment, metal is recovered (in its elemental form), as well as the chelating agent (in its tretraprotonated form). Both products are evident by visual inspection.

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