
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 electrodes¹, composite electrodes² and boron doped diamond film electrodes³. 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.

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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 miniaturization¹ 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.

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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.

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**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 lack 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 been 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 functionalized 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****MATHIEU ETIENNE, ALAIN WALCARIUS**

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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 decade¹. 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 films² and evaluated the interest of finely tuned porosity for improving the sensor response towards silver(I) detection³.

More recently, we developed an original pathway for the deposition of mesoporous (organo)silica thin films⁴. 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 properties⁵, and also on the electroanalytical performance of the modified electrode for copper(II) detection⁶.

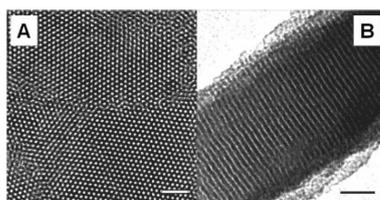


Fig. 1. SEM picture of electrodeposited mesoporous silica thin film. Scale bar is 20 nm

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

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The beginnings of nucleic acids (NA) electrochemistry were connected with application of polarographic techniques inherently employing the dropping mercury electrode. Oscillpolarographic, 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 elements¹. 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 seawater² and wine³). 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 discussed⁴. The existence of intermetallic compounds of Cu⁰ and Zn⁰ in the amalgam is well described in the literature⁵ 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 Cu⁰, Zn⁰ 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.

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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 aluminosilicates 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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Recently¹, standard potentials (E° , 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 ± 0.03 V for all redox couples except for halogens, which was 2.87 ± 0.01 V. 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°_{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° [V]	E°_{abs} [V]
Hydrogen electrode (NHE)	0.00	4.20
Calomel electrode		
• Hg/Hg ₂ Cl ₂ , KCl (1M) – NCE	0.28	4.48
• Hg/Hg ₂ Cl 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 ₂ SO ₄ , H ₂ SO ₄ (1M)	0.67	4.87
• Hg/Hg ₂ SO ₄ , K ₂ SO ₄ (saturated)	0.65	4.85
Silver / silver sulfate		
• Ag/Ag ₂ SO ₄ , H ₂ SO ₄ (1M)	0.71	4.91
• Ag/Ag ₂ SO ₄ , K ₂ SO 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 hydrogen³.

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 hydroxide⁴. 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 process².

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 VIIOLOGENS – THEIR ELECTRO-CHEMICAL AND ADSORPTION PROPERTIES ON MERCURY****VILIAM KOLIVOŠKA^a, MICHAL VALÁŠEK^b, LUBOMÍR POSPÍŠIL^a, MAGDALÉNA HROMADOVÁ^a**^a *J. Heyrovský Institute of Physical Chemistry of ASCR, v.v.i., Dolejškova 3, 18223 Prague,* ^b *Institute of Organic Chemistry and Biochemistry ASCR, v.v.i., Flemingovo n. 2, 166 10 Prague, Czech Republic*
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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 reduction 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 $\mu\text{F cm}^{-2}$ 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 $5.2 \times 10^{-11} \text{ mol cm}^{-2}$, 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.

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OP-13**10th DECEMBER 1959: JAROSLAV HEYROVSKÝ AND NOBEL PRIZE****JIŘÍ JINDRA***Cabinet of the History of Sciences, Institute for Contemporary History, v.v.i., Academy of Sciences of the Czech Republic, Vlašská 9, 118 40 Praha 1, Czech Republic*
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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****ROBERT KALVODA***J. Heyrovský Institute of Physical Chemistry, Academy of Science of the Czech Republic, v. v. i., Dolejškova 3, 182 23 Prague 8, Czech Republic*
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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 ELECTRO-CHEMICAL DETECTION OF BIOMOLECULES****ARKADY A. KARYAKIN, MIKHAIL Y. VAGIN***Chemistry faculty of M. V. Lomonosov Moscow State University, 119991 Moscow, Russia*
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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. Alterna-

tively, 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 porosity¹⁻³ or by using carbon nanotubes for their elaboration^{4,5}, with the ultimate "microelectrode" being actually a single nanotube addressable by an external field⁶. 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 detection¹. 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 damage¹.

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. Electrochemical impedance spectroscopy is used for the verification of changes at the DNA layer⁴. Antioxidative effects of standard chemicals and plant extracts are also detected.

This work was supported by the Applied Research Project of

the Ministry of Education of the Slovak Republic (AV/4/0103/06) and the Grant Agency VEGA (Project No. 1/0852/08).

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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 Gibbs¹. Roots are even older and are represented by “voltmeters”. 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 Kohlrausch². Nernst equation³ (1889) was the base for direct potentiometry, *e. g.*, determination of sparingly soluble electrolytes. Max Cremer⁴ is accredited as the inventor of the glass electrode (1906), which is the first electrochemical sensor. Potentiometric indication of titrations by Robert Behrend⁵ (1883) was the first instrumental indication in volumetric analysis.

The invention of polarography by Jaroslav Heyrovský⁶ (1922) is the starting point of wide application of electroanalysis with the dropping mercury electrode. The polarograph, developed in cooperation with Masuro Shikata⁷, 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 sensors⁸.

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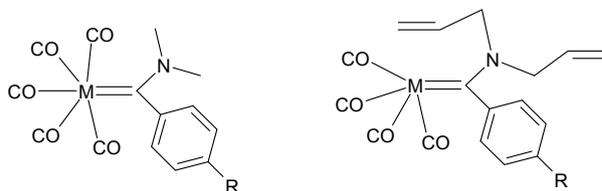
OP-19

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 = Cr¹, W, Fe) with or without chelating allyl 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.

This work was supported by the GA AV CR (grant IAA 400400813).

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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 thallium¹. 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 samples⁴. 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 years¹⁻⁴.

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 Na₂SO₄ 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 chronoamperometry 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-nitrosodinitrobenzenes (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 compari-

son 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 techniques³⁻⁵. 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 millivolts); 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.

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OP-24**LANGMUIR-BLODGETT FILMS OF NAFION: THE ROLE OF THE THIN FILM IN THE ELECTRO-CHEMILUMINESCENCE OF Ru(bpy)₃²⁺**

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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 come 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 microscopy¹, 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)₃²⁺ redox probe² in LB-Nafion coatings, deposited onto transparent ITO (indium-tin oxide) electrodes using tertiary amines as the co-reactant. 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 struc-

tures. 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 membranes¹⁻⁴, 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 solution⁵. The time variation corresponds to an increase in the membrane capacitance, *i.e.*, to thinning of the lipid structure¹.

The authors gratefully acknowledge financial support by the GA AV CR (No. IAA400400806).

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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 solution¹. 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 required². 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 experiments³.

The focus of this work is on the electrochemistry of hydrogen sulfide (H₂S) gas, which is of major importance in the petrochemical industry, and whose toxicity has necessitated the development of monitoring devices. Separation of H₂S 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 extraction¹.

H₂S 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 laboratory¹. 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 pathogenic 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 electrodes¹. 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 sequences². 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 ASSESSMENT 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 LMWOAs¹. The main type of the ligand is oxalic acid mostly exuded by willow or penny-cress². 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.

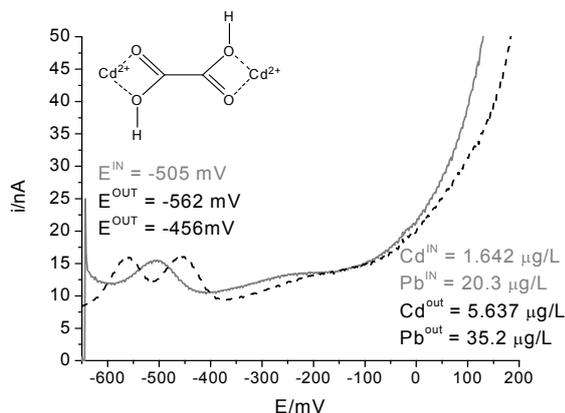


Fig. 1. **The voltammogram** (ASV-HMDE, vs. Ag/AgCl/3M KCl, $t = 120$ s, $E_{ac} = -900$ mV), and designed structure of one of the cadmium-oxalic acid complexes

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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 ($Fe^{II} \rightarrow Fe^{III}$) whereas in acetonitrile the reduction of catalyst ($Fe^{III} \rightarrow Fe^{II}$) 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 scan³. 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} complex⁴.

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****ROMANA SOKOLOVÁ^a, LUBOMÍR POSPÍŠIL^b,
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The study of the reductive cleavage of carbon-heteroatom bond in halogenated organic compounds is proposed. The chlorinated triazines¹, chlorinated dicarboximides^{2,3} and halogenated benzonitriles⁴ 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) mechanism⁷. 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****ANCA-IULIA STOICA^a, SONIA CENTI^b, MARCO
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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 detection¹.

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****MIKOLAJ DONTEN, MARIANNA GNIADK,
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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 synthe-

sized 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 detect-

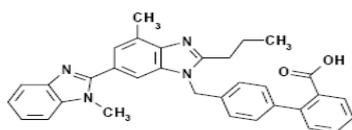


Fig. 1. Chemical structure of Telmisartan

ing TS that requires no such procedures is, thus, highly desirable from a practical viewpoint.

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 method¹) is the technique, based on calculation of the quantity of electricity Q_{∞} , which corresponds to the whole substance conversion, using the following expression

$$Q_{\infty} = \frac{Q_t}{1 - 10^{-kt}} \quad (1)$$

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

In accordance to the formula for coulometric constant

$$k = \frac{DS}{\delta V} \quad (2)$$

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:

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

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 determina-

tion 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 glycerol³. 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 reported⁴.

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 B₁₂ 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 B₁₂ 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 B₁₂ 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 B₁₂ in pharmaceutical products.

This work was supported by Slovak Research and Development Agency under the contract No. APVV-0057-06 and VEGA grant No.1/0066/09.

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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 (FeCp₂) as catalyst¹. 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 employed³. FeCp₂ 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 FeCp₂⁺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 FeCp₂ 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 alkylthiols 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 detection¹.

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 cations 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 targets². 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 occurring in nucleic acids possess 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 earth³. 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 now. However, recently we have found that 2D condensation can be observed with certain homopyrimidine oligodeoxynucleotides⁶ at negatively charged mercury electrode surface. DNA adsorption at the electrode surfaces is of fundamental interest for the development of DNA-based biosensors⁷.

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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 graphite¹, electrochemical oxidation of graphite², proton-beam irradiation of nanodiamonds³ 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 electrochemiluminescence 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 PtCl₄²⁻ on the MWNTs' sidewalls. Deposition of Pt NPs on the MWNTs' sidewalls was realized by in situ chemical reduction of anionic ions PtCl₄²⁻ 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 decompose³. The use of carbon paste electrodes in analysis of organic compound will be documented on selected examples of environmental and pharmaceutical applications³. 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 ELECTROCHEMICAL DETERMINATIONS

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Graphene is a new member to the family of carbon nano-scaled materials¹ 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 materials⁵.

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 ($\text{pH} > \text{p}K_{\text{a, chitosan}}$). 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 Chitosan-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****EVGENIA DMITRIEVA, LOTHAR DUNSCH***

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The modern techniques of spectroelectrochemistry are used for the analysis 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 chains¹. The role of the phenazine structure in the stabilization of charged states in polyaniline was studied by *in situ* ESR-UV/vis-NIR spectroelectrochemistry² 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.

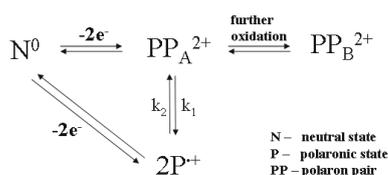


Fig. 1. Scheme of the formation of charged states upon electrochemical oxidation of polyaniline

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OP-48**MONOCRYSTALLINE DIAMOND PASTE BASED SENSORS AND MICROSENSORS****RALUCA-IOANA VAN STADEN, JACOBUS FREDERICK VAN STADEN**

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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****JACOBUS FREDERICK VAN STADEN, RALUCA-IOANA VAN STADEN**

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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-T₃, L-T₄ and D-T₄ 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 microcapil-

lary-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.