ORAL PRESENTATIONS

OP01
VISUALISATION OF THE CATALYTIC ACTIVTY OF ENZYME-REDOXPOLYMER SPOTS FOR OPTIMISATION OF A BIOFUEL CELL CATHODE USING REDOX COPMTETITION SCANNING ELECTROCHEMICAL MICROSCOPY (RC-SECM)

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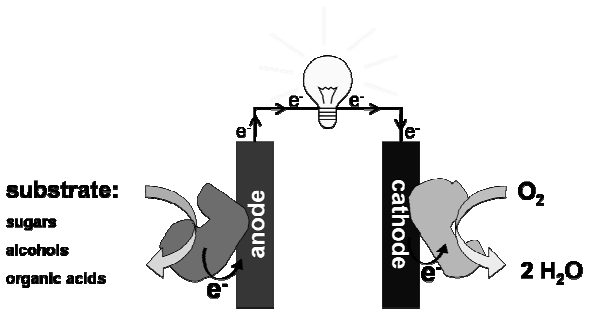
Biofuel cells are power generating devices which use environmental friendly fuels like sugars, alcohols, organic acids or oxygen at anode and cathode, respectively. The reactions at both electrodes are catalysed by biocatalysts such as enzymes or whole organisms. In addition, redox mediators are often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

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

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



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

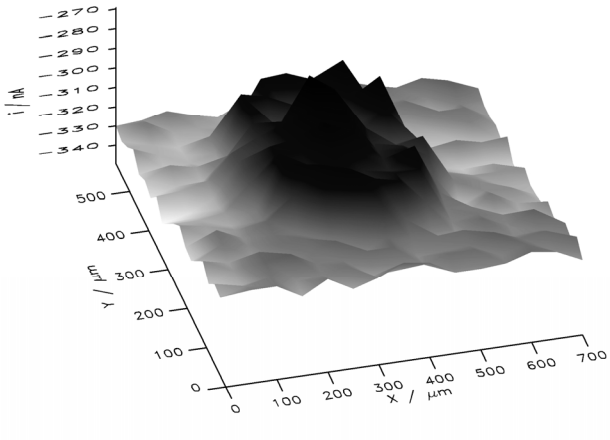


Fig. 1. **3D RC-SECM picture of a laccase-redox polymer spot**. Darker areas represent higher catalytic acti-vity at the sample

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OP02
ELECTROCATALYTIC ACTIVITY OF ITO ELECTRODES MODIFIED WITH METAL NANOPARTICLES

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In recent years, the surface modification of electrodes with metal nanoparticles (NPs) has led to some of the latest

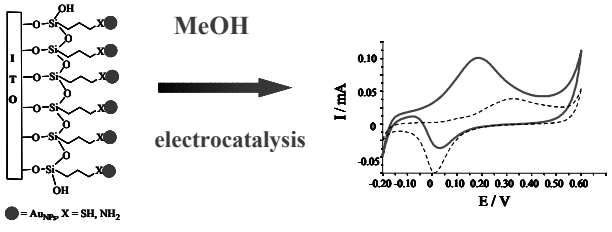
developments in the field of electrochemical sensors. To date gold nanoparticles (AuNPs) are the most extensively studied because of their unique size-dependent physical, optical and electronic properties when compared to bulk gold[1]. Moreover, also platinum nanoparticles (PtNPs) have evoked increasing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

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

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

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

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



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

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OP03
NEW ELECTRODE MATERIALS FOR DETERMINATION OF GENOTOXIC SUBSTANCES

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There is an ever increasing demand for the determination of extremely low concentrations of various genotoxic substances in complex environmental or biological matrices. Modern voltammetric and amperometric techniques can be used for determination of electrochemically reducible or oxidisable genotoxic substances because of their high sensitivity, sufficient selectivity (especially in combination with a suitable preliminary separation) and low cost, which make them suitable for large-scale monitoring[1]. There is a constant search for new electrode materials suitable for this challenging task. We will report our recent result regarding the determination of submicromolar and nanomolar concentrations of electrochemically reducible genotoxic substances with various types of amalgam electrodes[2] (meniscus modified silver solid amalgam electrode, silver solid composite amalgam electrode, amalgam paste electrode based either on mixture of solid silver amalgam with a suitable organic pasting liquid or on silver amalgam paste containing lower amount of silver) and on boron doped diamond film electrode[3]. Moreover, we will

report our results regarding voltammetric and amperometric determination of electrochemically oxidisable genotoxic substances (e.g. aromatic or heterocyclic hydroxy or amino compounds) both on boron doped diamond film electrodes and carbon paste electrodes based on glassy carbon micro beads, which are compatible with high content of organic solvent in measured solutions[4]. Attention will be paid to electrochemical pretreatment, renewal of the electrode surface and to other procedures minimizing problems with electrode passivation which prevent broader use of electroanalytical methods in practice.

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OP04
LIQUID CRYSTALLINE CUBIC PHASES FOR HOSTING ENZYMES - FROM BIOELECTRODES TO BIOFUEL CELLS

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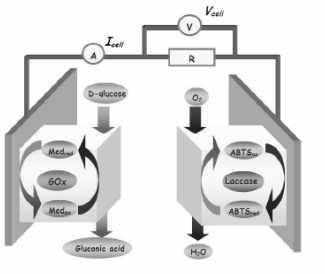
Lipid liquid-crystalline cubic phases are naturally fitted with a network of water channels by which substrate and product of catalytic reactions can be transported. Monoolein liquid-crystalline films are proposed as a convenient matrix to fix biocatalysts at the electrode surfaces. The material keeps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

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



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

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OP05
ELECTROANALYSIS: NANOPARTICLES AS MODIFIERS AND MARKERS

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

Magnetic nanoparticles were employed in immunoassay with magnetic separation.

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

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

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

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OP06
MEASUREMENT OF BISPHENOL A IN RIVER WATER USING SCREEN-PRINTED CARBON ELECTRODE USING CATIONIC SURFACTANT

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

Bisphenol A (BPA) 1×10^{-4} mol L^{-1} is oxidized at 0.5 V on the screen-printed carbon electrode, which height intensity is duplicated in the presence of 7.5×10^{-4} mol L^{-1} of CTAB, as shown Fig.1. The effect was evaluated for different proportion of CTAB/BPA and the peak height increases up to [CTAB]/[bisfenol A] 2:1. The peak is dramatically decreased at higher concentration when the system reaches the critical micelar concentration. So, all the further studies were carried out for maximum proportion of [CTAB]/[bisfenol A] 2:1.

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

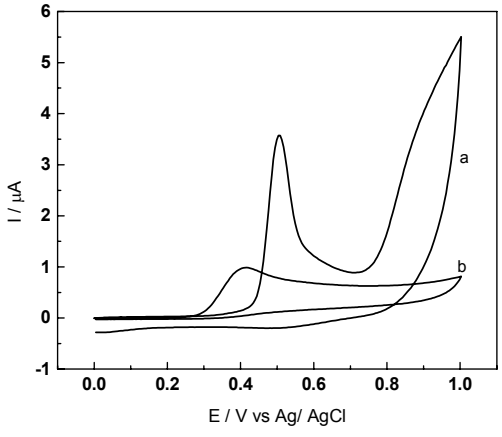

Fig. 1. **Cyclic voltammograms** obtained for 1×10^{-4} mol L^{-1} of BPA in Britton-Robison buffer (pH 7) on screen- printed carbon electrodes (a) without and (b) with 7.5×10^{-4} mol L^{-1} CTAB surfactant. Scan rate: 100 mVs^{-1}

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

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

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

Acknowledgement: Capes, Fapesp and CNPq.

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OP07
FLOW-THROUGH CHRONOPOTENTIOMETRY IN PROCESS ANALYTICAL CHEMISTRY

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

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

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OP08
HAEM PROTEINS IN NON-AQUEOUS SOLVENTS: ELECTROCHEMISTRY, STRUCTURE AND CATALYSIS

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

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

cernible trends evident between solvents.

Funding from SFI, Enterprise Ireland and IRCSET is gratefully acknowledged.

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OP09
SMOOTH AND MESOPOROUS Pt MICRO-ELECTRODES MODIFIED BY UPD Bi FOR THE DETECTION OF TRACE METALS AND SMALL ORGANIC MOLECULES

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

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

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

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

OP10
ELECTROANALYSIS WITH NANOELECTRODE ENSEMBLES IN ROOM TEMPERATURE IONIC LIQUID

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

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

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

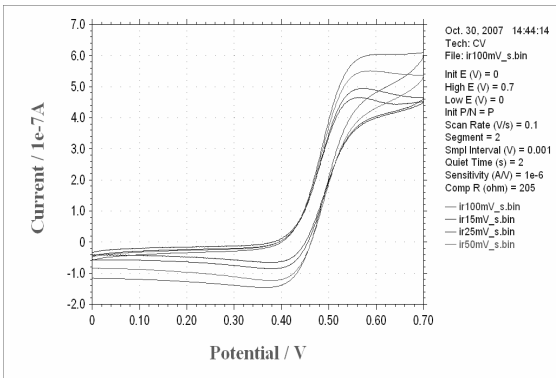

Fig. 1. **Cyclic voltammograms recorded at different scan rates** (from 15 to 100 mV s^{-1}) at NEE in 10^{-3} M ferrocene, BmIm(N(Tf)$_2$) solution

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

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

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OP11
MAGNETIC NANOPARTICALS PLAY AN IMPORTANT ROLE IN ELECTROANALYTICAL CHEMISTRY

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

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

Financial support from NSFC is greatly appreciated.

OP12
ELECTROCHEMICALSENSORS BASED ON ORGANIC ELECTROCHEMICAL TRANSISTORS

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

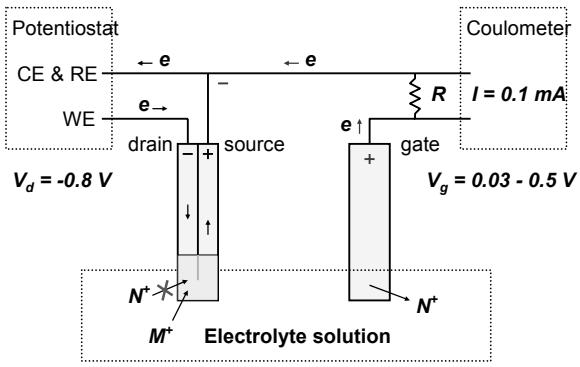

Fig. 1. **Experimental set-up for the measurement**

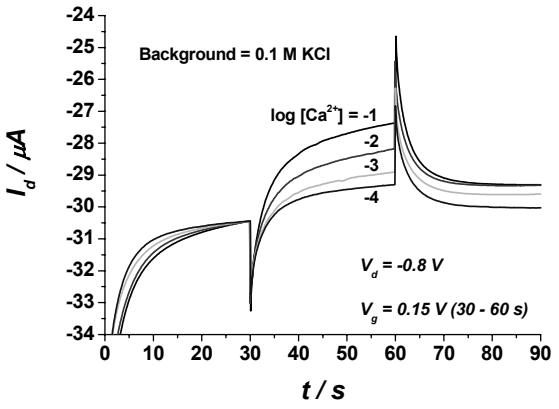

Fig. 2. **Transistor response on changes in $[Ca^{2+}]$ in the sample solution**

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

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

This work is part of the activities of the Åbo Akademi University Process Chemistry Centre. Professor Magnus Berggren, and his research group from University of Linköping, Sweden are acknowledged for the transistor substrates.

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OP13
MONITORING HEAVY METALS IN SEAWATER BY ELECTROCHEMICALLY INDUCED DEPOSITION AS HYDROXIDES

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

OP14
LABEL-FREE ELECTRICAL DETECTION OF PROTEIN INTERACTIONS WITH PEPTIDE APTAMERS

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

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

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

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

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OP15
N-NITROSOAMINES AS REAGENTS FOR THE CONTROLLED RELEASE OF NITRIC OXIDE VIA DISSOCIATIVE ELECTRON TRANSFER

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

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OP16
CONSTRUCTION OF ELECTROCHEMICALLY LABELED OLIGONUCLEOTIDES AND THEIR USE IN ANALYSIS OF NUCLEOTIDE SEQUENCES AND PROBING OF DNA-PROTEIN INTERACTIONS

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

The Os,L react selectively with thymine residue in single-stranded DNA under physiological conditions, forming covalent electroactive adducts. ON probes modified with Os,L bearing different ligands (L) differ in their peak potentials which has been utilized in electrochemical "multicolor" DNA sensing[2]. Deoxynucleoside triphosphate (dNTP) conjugates with various electroactive moieties (such as ferrocene[3], amino or nitro phenyl groups[4]), attached to the nucleobase, have been prepared via aqueous-phase cross-coupling reactions. These dNTP can easily be incorporated in ON sequence-specifically by primer extension. Due to electronic

conjugation via unsaturated (ethinyl) bridge, electrochemical properties of these labels depend on the coupled nucleobase and respond to incorporation into DNA. We have applied this labeling strategy, in connection with magnetoseparation techniques[1], for the detection of single nucleotide polymorphisms, probing abundance of a specific nucleobase in a target DNA stretch, as well as in monitoring of DNA-protein interactions.

This work was supported by GACR (203/07/1195), GA ASCR (IAA500040701) and MEYS CR (LC06035).

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OP17
DIFFERENTIAL ELECTROLYTIC POTENTIOMETRIC, A DETECTOR FOR FIA DETERMINATION OF VITAMIN C IN PHARMACEUTICAL PREPARATIONS

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

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

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

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

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

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

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OP18
NOVEL APPROACHES IN THE DEVELOPMENT OF AMPEROMETRIC IMMUNOSENSORS FOR THE DETERMINATION OF *Staphylococcus aureus*: PEROXIDASE-LABELLED SYSTEMS BASED ON DTSP-MODIFIED GOLD ELECTRODES

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

The sensor fabricated with antiRbIgG-HRP gave the best analytical characteristics with a limit of detection of 3.42×10^5 cells mL^{-1}. The repeatability of the measurements with the same immunosensor and the reproducibility of the responses obtained with different immunosensors were 7.3 % and 9.1 % respectively.

In order to improve sensitivity cells wall lysis was assayed using two procedures: heat and ultrasonic treatments. These processes produced the breaking of bacteria and the availability of many more protein A-bearing cell portions[2]. In the most favourable experimental conditions, after cell wall lyses by ultrasonic treatment, a decrease of one order of magnitude in the detection limit was achieved, now being possible to detect 1.25×10^4 cells mL^{-1}.

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OP19
APTASENSORS FOR SMALL MOLECULES: A COMPETITIVE IMPEDIMETRIC ASSAY FOR THE DETECTION OF AMINOGLYCOSIDE ANTIBIOTICS

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

tobramycin and neomycin B[1].

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

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

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OP20
BIOSENSORS AND BIOFUEL CELL ANODES BASED ON NEW SUGAR OXIDISING REDOX ENZYMES

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

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

The authors thank the following organisations for financial support: The Swedish Research Council, The Austrian Science Fund (Fonds zur Förderung der wissenschaftlichen Forschung), translational project FWF.

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OP21
CHARACTERISATION OF NEW CARBON FILM ELECTRODES FOR ELECTROCHEMICAL SENSORS

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The electrochemical, morphological and microstructural properties of carbon film electrodes made from carbon film electrical resistors of several different nominal resistances from 1.5 Ω up to 2 kΩ have been investigated before and after cycling in perchloric acid or electrochemical pre-treatment at +0.9 V *vs* SCE and integrated with previous studies on 2 Ω

carbon film resistor electrodes[1,2]. Comparison has also been done with other types of carbon electrode, such as glassy carbon, carbon composite and at carbon films deposited on piezoelectric quartz crystals.

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

Future applications and perspectives will be discussed.

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OP22
VOLTAMMETRIC CONTROL OF HOMEOSTASIS OF HUMAN METABOLISM

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

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

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OP23
ANTIMONY FILM ELECTRODE FOR ELECTROCHEMICAL STRIPPING MEASUREMENT OF TRACE HEAVY METALS

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

anodic stripping analysis of trace heavy metals, which revealed attractive electroanalytical performance[2].

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

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OP24
URANIUM SORPTION ONTO SIDERITE IN CARBONATE MIXTURES

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

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

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

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

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

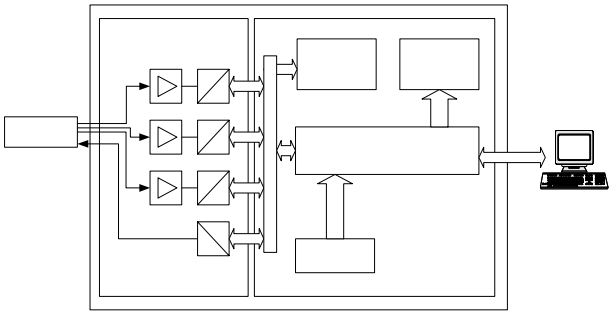

Fig. 1. **Schematic diagram of the measurement device**

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OP26
HETEROGENEOUS CARBON ELECTRODES

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Heterogeneous carbon electrodes are characterized by embedment of electrically conductive carbon particles

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

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

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

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

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OP27
ACHIEVEMENT OF LIMITING PERFORMANCE CHARACTERISTICS OF THE ENZYMES IN DIRECT BIOELECTROCATALYSIS

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

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

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

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

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OP28
POLYANILINE NANOSTRUCTURES AND THEIR APPLICATIONS TO CHEMICAL SENSORS AND BIOSENSORS

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We present methods for the nanostructuring of conducting polymer, polyaniline (PANI) and their application to electrochemical sensing. Before electrochemical polymerization of aniline, the surface of each electrode was modified with polystyrene (PS) templates to form monolayer or multi-layer films. PS nanoparticles of different size have been used to investigate the behaviour of films with different nanodimensions The charge of the template particles has also been used to control the mechanism of PANI growth. On electrodes modified with negatively charged PS nanoparticles, PANI has been found to grow around the template particles to form PS-PANI core-shell nanostructures. When negatively charged PS

templates were used, the electropolymerized PANI grew from the surface of the electrode into the interstitial spaces between the PS to form PANI-PS nanocomposites. Further structures can be derived by the dissolution of the PS template to form hollow spheres or porous films, respectively. Additionally, PANI films with multiple orders of micro- and nanostructure have been prepared to create highly nodular, "cauliflower-like" nanostructures with high surface area. The morphology of these films has been confirmed by scanning electron microscopy.

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

OP29
CHARGE TRANSFER RESISTANCE MODELLING FOR OPTIMIZATION OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY DNA DETECTION

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

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

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

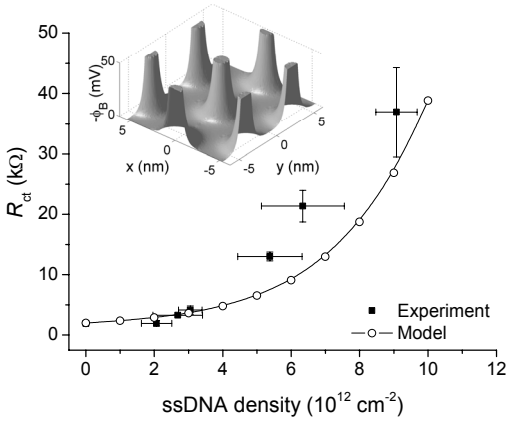

Fig. 1. **Comparison of experimental and calculated R_{ct} variation with ssDNA probe density, for I = 447 mM**. Error bars show the mean and spread of 3 samples. Inset: potential barrier for 3×10^{12} cm^{-2} ssDNA

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

OP30
QUANTIFICATION OF ELECTROACTIVE MOLECULES USING A SERIAL DILUTION MICROFLUIDIC SYSTEM

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

Electrochemical detection methods are more and more implemented on lab-on-a-chip devices due to their inherent ease of miniaturization, low power requirements, low limits of detection and compatibility with microfabrication technologi-

es[4,5]. Moreover, electrochemistry presents a unique advantage compared to optical techniques (such as UV detection) that is the possibility of downsizing the detection window without loss of performance. Using electrochemical detection, it is possible to reach nM limits of detection[6] but also to carry out experiments *on-site* by using a portable device[7]. However, this detection technique presents also serious drawbacks that are inherent to the technique such as the need to have electroactive species and the fouling of the electrodes.

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

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

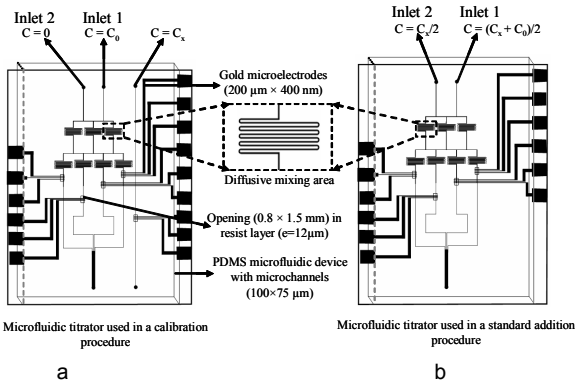

Fig. 1. **Schematic representation of the microfluidic structure made of PDMS that was used to quantify sample concentration using either an on-chip calibration curve (a) or a standard addition procedure (b)**. Each microchannel embedded in the PDMS slab was 100 µm wide and 80 µm deep. Electrode network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

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

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OP31
INTEGRATED BIOELECTROCATALYTIC SYSTEMS COMPOSED OF CARBON NANOTUBE-SUPPORTED MEDIATORS, ENZYMES AND METAL-LOPORHYRINS

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We have exploited here unique electronic and mechanical characteristics of multi-walled carbon nanotubes (MCNT) to construct the efficient anodic glucose oxidase based bioelectrocatalytic system. First, MCNTs have been modified with ultra-thin layers of tetrathiafulvalene (TTF) to form stable colloidal suspensions of carbon nanostructures. They have been utilized to produce Nafion-containing inks for sequential deposition of components. The presence of TTF is expected to facilitate an effective flow of electrons from the redox centers of glucose oxidase to the glassy carbon electrode. TTF and its derivatives constitute a group of redox molecules that were successfully used as redox mediators in the enzyme electrochemistry. As before, MCNTs have supported transport of

electrons within the bio-electrocatalytic film. Our highly MCNT-based porous films have presumably acted as three-dimensional network of nanowires around the enzyme molecules and have promoted the efficient electron transfers. Thus we have produced a catalytic system capable of effective oxidation of glucose in 0.1 M phosphate buffer (pH 7).

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

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

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

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

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

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

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

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

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

As first assay model, an indirect competitive assay format was carried out. The microchannels were used as solid-phase for rIgG immobilisation; then, a competition between an unknown amount of free rIgG and a fixed concentration of anti-rIgGalkaline phosphatase labelled was created directly in the modified channels. Finally, the substrate solution (paminophenyl phosphate 10 mM) was introduced and a real

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

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

OP34
TAILORING SURFACES AND SUPPORTS FOR ENZYME MEDIATION, WITH APPLICATION TO BIOSENSOR AND BIOPOWER DEVICE DEVELOPMENT

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

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

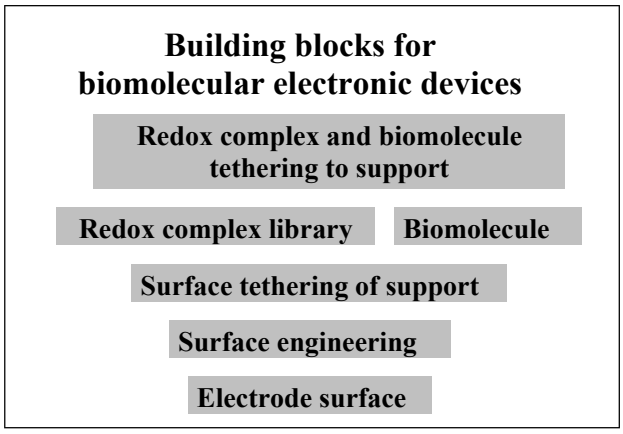

Fig. 1. **Schematic depiction of the toolbox available for rational design and optimization of electrode surfaces and supports to provide bioelectrochemical devices**

OP35
SILICATE CONFINED IONIC LIQUID FOR ELECTRODE MODIFICATION

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

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

covered by ionic liquid precursor. The repelling of $Ru(NH_3)_6^{3+}$ cations by this electrode is also demonstrated.

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

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OP36
MANGANESE DETECTION IN RIVER WATER BY ANODIC STRIPPING VOLTAMETRY USING ROTATING Hg-Ag AMALGAM ELECTRODE

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

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

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

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OP37
THE USE OF IMPEDANCE SPECTROSCOPY FOR THE DETECTION OF DNA AND ANTIBODIES BASED ON RESTRICTED CHARGE TRANSFER

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

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

For a gold chip electrode and immobilised ss-DNA (ref.[2]) only a small increase was found for the interfacial capacitance after ds formation (~5 %), however the charge transfer resistance R_{ct} increased by a factor of about three for an 18-mer oligonucleotide. The relative change of R_{ct} can be used for a sensorial DNA detection. There is a considerable influence of the ionic strength on the measurement. Sensitiv-

ity for oligonucleotides in the nanomolar concentration range can be achieved. Length of the DNA was varied here from a 18mer to a 37mer. Binding of organic dyes of different charge underline the idea that the changed charge situation at the sensor surface govern the impedimetric response upon hybridisation.

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

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OP38
ASSESMENT OF FREE RADICALS POTENTIAL TOXICITY USING LIPOPROTEIN BIO-MIMETIC SYSTEMS

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

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

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

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OP39
INTRAMOLECULAR ELECTRONIC INTERACTIONS IN TWO TYPES OF DICARBONYL COMPOUNDS AND THEIR DERIVATIVES – AN ELECTRO-CHEMICAL AND QUANTUM CHEMICAL STUDY

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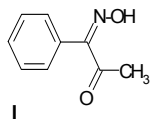
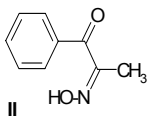
Molecules with two (or more) redox centers that are vicinal or connected by an unsaturated bridge, due to the intramolecular electronic interactions, exhibit often special redox properties that do not correspond to the sum of original characteristic properties of each of the centers. The most recent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

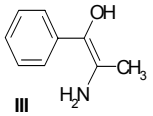
The reduction of 1-phenyl-2-oxo-1-oximinopropane (***I***) in acidic media follows the expectable pathway common for most oximes (i.e. a four-electron reduction yielding the corresponding α-aminoketone which is further reduced to the benzyl methyl ketone). The isomeric 1-phenyl-1-oxo-2-oximinopropane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



I



II



III

further converted to the tautomeric α-aminoketone.

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

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

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

This work is supported by the CZ-US project KONTAKT (MSMT, N°. 1P05ME785).

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OP40
MONITORING OF NON-IONIC SURFACTANTS IN THE AQUATIC ENVIRONMENT THROUGH THEIR ENTRAPMENT IN A PTFE CAPILLARY TRAP AND INDIRECT TENSAMMETRIC DETERMINATION

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

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

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

OP41
SURFACE, ELECTROCHEMICAL AND ELECTRO-ANALYTICAL PROPERTIES OF POLYMER MODIFIED ELECTRODES

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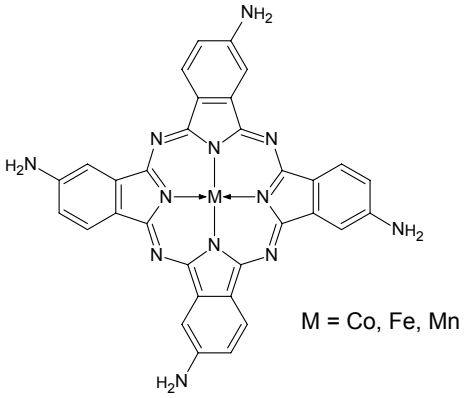
The quest to find new and stable materials that can be used to modify electrodes is of interest. This is due to the fact that the modified electrode systems have been found to yield very important analytical devices for various electrochemical



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

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

This work is funded by Project AuTEK (MINTEK), DST/ MINTEK Nanotechnology Innovation Centre(NIC) and DST under Research Professional Development Programme.

OP42
RESPONSE BEHAVIOUR OF AMPEROMETRIC GLUCOSE BIOSENSORS BASED ON DIFFERENT CARBON SUBSTRATE TRANSDUCERS COATED WITH ENZYME-ACTIVE POLYMER LAYER: A COMPARATIVE STUDY

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

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

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OP43
DETECTION OF INFLUENZA VIRUS A BY USING IMPEDIMETRIC BIOSENSOR

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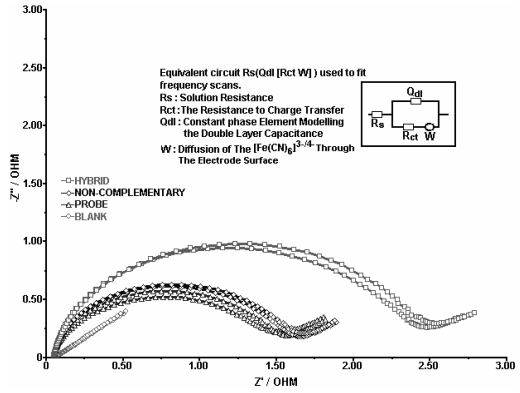
In this study, label free DNA probe sequences related to the influenza type A virus and its complementary target sequences were detected by monitoring the changes in surface impedance of the pencil graphite electrode (PGE), before and after hybridization process. The analysis of the hybridization behaviour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



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

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

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OP44
PCR-COUPLED ELECTROCHEMICAL DETECTION OF *Legionella pneumophila*

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

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

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

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

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OP45
VOLTAMMETRIC SIGNALS CALCULATED BY INFINITE SERIES APPROACH

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

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

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

sion coefficients of intercalated ions, which in general are considerably smaler compared to their values in the solution.

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

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OP46
REDOX ACTIVE LAYERED DOUBLE HYDROXIDES FOR GLUCOSE BIOSENSOR DEVELOPMENT

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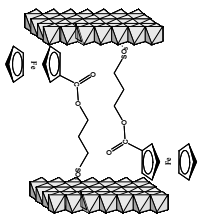
Layered double hydroxides (LDH) are a family of synthetic lamellar materials with interlayer space containing anions. Organic electroactive anions such, 2,2'-azinobis 3-ethyl--benzothiazoline-6-sulfonate (ABTS) and anthraquinone sulfonate have been intercalated within LDH interlayer domain, giving well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

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

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

Configurations of Gox biosensors



Scheme of ZnCr-FcPS

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OP47
OH-CHIP IMPEDIMETRIC DETECTION OF VIABLE PATHOGEN BACTERIA

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

Bacteria are small prokaryotic and unicellular microorganisms with a huge variety resources adapt to any metabolic

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

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

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

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

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

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

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OP48

SENSORS BASED ON SOLID COMPOSITES IN ELECTROCHEMISTRY OF BIOLOGICALLY ACTIVE COMPOUNDS

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

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