

PP085**TOWARDS Q-PCR OF *Escherichia coli* WITH IMPROVED ELECTROCHEMICAL DETECTION****ANABEL LERMO^a, SUSANA CAMPOY^b, JORDI BARBÉ^b, SALVADOR ALEGRET^a, and MARIA ISABEL PIVIDORI^{a*}**

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Outbreaks of foodborne disease caused by *E. coli* bacteria have become a serious problem. While there are many types of *E. coli* bacteria, only certain types are caused of important foodborne illness, as the harmful foodborne strain called O157:H7. These pathogenic strains of *E. coli* are found in undercooked meat, lettuce, unpasteurized milk, apple juice and contaminated well water¹. In food and environmental samples responsible for disease, the levels of contamination are sometimes very low. Thus, very sensitive detection methods are required.

A very sensitive assay for the electrochemical detection of *Escherichia coli* based on DNA biosensors has been designed. The electrochemical detection is performed by the specific amplification of the *eaeA* gene, related with the pathogenic activity of these bacteria. The amplification is performed by Polymerase Chain Reaction (PCR) using labelled primers with biotin and digoxigenin, obtaining a double labelled amplicon with biotin and digoxigenin in each extreme, respectively. The amplified biological material is detected by two strategies based on *i*) bulk-modified composite with avidin as affinity biomolecule, obtaining high selective electrodes²; and *ii*) magneto sensors³. In the first approach, the double-labelled amplicon *i*) is directly linked to the avidin-modified biocomposite while in the second approach *ii*) it is previously immobilized on magnetic beads modified with streptavidin, followed by the magnetic capture of the beads by the magneto sensor. The electrochemical detection is finally achieved by an enzyme marker, based on HRP.

The combination of the genome amplification by PCR, capture of the double-tagged amplicon and electrochemical detection using a sensitive m-GEC electrode, provide promising results compared with Q-PCR based on TaqMan probes.

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PP086**ELECTROCHEMICAL MAGNETO IMMUNO-SENSING AND GENOSENSING FOR FOOD SAFETY****A. LERMO^a, E. ZACCO^a, S. LIÉBANA^a, S. FABIANO^b, S. HERNANDEZ^b, S. ALEGRET^a, and M. I. PIVIDORI^{a*}**

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In recent years, a number of food-safety emergencies have shaken consumer confidence in the production of food and have focused attention on the way food is produced, processed, and marketed. Most of the agents found in food are natural contaminants from environmental sources, but some are deliberate additives. Although microbiological issues are the greatest concern¹, many consumers are worried about the long-term impact of mixtures of chemicals additives (such as pesticides and veterinary drug residues)². As food regulatory agencies have established strict control programs in order to avoid food contaminants from entering the food supply, official laboratories should be able to efficiently process a high number of samples. As a result, routine, rapid and efficient food control becomes mandatory. Biosensors offer an exciting alternative to the more traditional methods for food analyses, allowing rapid 'real-time' and multiple analyses that are essential for the detection of contaminants in food³.

One of the most promising materials is biologically modified magnetic beads based on the concept of magnetic bioseparation. Magnetic beads have brought novel capabilities to electrochemical immunosensing and genosensing. The development of magneto immunosensing and genosensing strategies with electrochemical detection is presented in this work. The strategy can be used to detect by immunological recognition pattern, pesticides, antibiotic residues, or can also be used to detect pathogenic bacteria or viruses such as *Salmonella*, *E.coli* or *Hepatitis*. The biological reaction for these assays was performed on magnetic beads and the electrochemical detection was based on HRP enzyme. In all cases, the modified magnetic beads were then attached to a novel magneto sensor based on graphite-epoxy composite for the electrochemical detection. These new assays offer great promises for rapid, cost-effective and on-site analysis of biological, food and environmental samples.

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PP087**DISPOSABLE MAGNETIC DNA SENSORS FOR THE DETERMINATION OF A SPECIFIC *Enterobacteriaceae* FAMILY GENE****OSCAR A. LOAIZA, SUSANA CAMPUZANO, MARÍA PEDRERO, and JOSÉ M. PINGARRÓN***

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DNA sensors combined with magnetic separation constitute a time saving approach which may replace current lengthy enrichment protocols, also allowing the application of diverse end-point detection methods.

In this study, an enzyme-amplified strategy based on the coupling of streptavidin-peroxidase to biotinylated *lac z* gene target sequences has been developed. Previously, the biotinylated 25 mer capture probe was attached to streptavidin-modified magnetic beads, which were then immobilised at the surface of TTF modified screen printed gold electrodes (Au/SPE).

Amplification of the electrochemical signal was achieved coupling a ultrasensitive streptavidin-peroxidase polymer to the biotinylated target, after the hybridisation step and using TTF as redox mediator. The amperometric response obtained at -0.15 V after the addition of hydrogen peroxide was used to detect the hybridization process. In order to improve the sensitivity of the determination and reduce the assay time, different variables of the assay protocol were optimized. The stability and analytical characteristics of the sensor were evaluated and compared with those obtained in a previous work¹. A low detection limit (5.7 fmol) with good stability ($RSD_{n=10} = 7.1\%$) was obtained. The obtained results show the ability of the sensor for the detection of low amounts of target oligonucleotide, which is an advantage in the determination of microorganisms without the need of PCR amplification. The developed magnetic DNA sensor was used for the detection of *E. coli* in cell cultures with good results.

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PP088**NEW STRATEGY FOR SNPs DETECTION USING AN ELECTROCHEMICAL GENOSENSOR ARRAY****FAUSTO LUCARELLI, GIOVANNA MARRAZZA*, and MARCO MASCINI**

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This communication describes development and characterization of an electrochemical genosensing platform where genotyping of clinically relevant samples relied on an unusual hybridization strategy: the stacking hybridization.

Taking advantage from the peculiar interactions existing between two coaxially hybridized oligonucleotides, which respectively served as stabilizing oligo and allele-specific oligonucleotide (ASO) probe, this method allowed the unambiguous resolution of mismatched from matched duplexes (yes or not response).

All hybridization experiments were performed at capture probe-modified screen-printed gold arrays^{1,2}. Accordingly, electrochemical transduction of the hybridization events was accomplished using a specific enzyme label, which converted its electro-inactive substrate into an electroactive derivative.

While optimizing the hybridization methodology, the performance characteristics of different pairs of coaxially hybridized probes were compared. The influence of parameters such as ASO probe length, relative position of the mismatched site and strength of the stacking interactions thus emerged.

Further characterization of the stacking hybridization process through melting experiments allowed a deeper understanding of how the mutual interactions between the oligos involved in the biorecognition process influenced selectivity and sensitivity of the assay.

To prove usefulness and general validity of the genotyping methodology, application of the analytical pathway was then demonstrated for human *TP53* gene.

Owing to its inherent selectivity, sensitivity and low cost, the proposed genotyping platform, implemented into an 8 electrodes array, thus represent a promising tool for the systematic screening of genes with mutational hotspots.

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PP089**TESTING OF BIODEGRADABILITY OF NON-IONIC SURFACTANTS USING THE INDIRECT TENSAMMETRIC TECHNIQUE COMBINED WITH A PTFE CAPILLARY TRAP****ZENON LUKASZEWSKI*, DOBROCHNA GINTER, ALEKSANDRA CHOLDERNA-ODACHOWSKA, LILIANA PIWOWARCZYK, ROBERT RYDLICHOWSKI, and BOGDAN WYRWAS**

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The widespread use of detergents means that complete biodegradation of their main components – surfactants – is necessary. Different tests are used for investigating biodegradability. In screening tests, an investigated surfactant is the sole source of organic carbon, and a very simple biodegradation progress control such as CO₂ production, total organic

carbon concentration or biological oxygen demand is sufficient. However in more complex cases, such as the continuous flow activated sludge test, a specific determination of the tested surfactant is necessary. This is very difficult in the case of non-ionic surfactants (NS), especially those without chromophoric groups such as oxyethylated alcohols. Use of the indirect tensammetric technique (ITT) combined with the PTFE capillary trap (PTFECT) significantly reduces such difficulties.

For NS determination, a small sample of a test effluent is pneumatically forced through a PTFECT, and the entrapped NS are eluted with ethyl acetate and determined using ITT with ethyl acetate as a monitor.

In order to demonstrate the potential of the proposed method, the biodegradability of oxyethylated alcohol C12E10 was tested under the conditions of the OCDE 301 test with activated sludge as inoculum. The concentration of C12E10 was determined daily. On the day of maximum biodegradation rate, the bacteria strain *Pseudomonas fluorescens* was isolated from the tested mixture. These bacteria were augmented, and the test of C12E10 biodegradation was repeated with the augmented *Pseudomonas fluorescens* as the inoculum. Immediate biodegradation of C12E10 was observed.

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PP090

INVESTIGATION OF THE MOBILITY OF THALLIUM IN THE ENVIRONMENT USING FLOW-INJECTION DIFFERENTIAL – PULSE ANODIC STRIPPING VOLTAMMETRY

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Thallium is an element which is highly toxic to humans, animals, micro-organisms and plants. The toxic effect of the element is closely related to its mobility. The main sources of thallium pollution are pyrites and lead-zinc ores. It is therefore the areas where these ores are mined and processed which are at the greatest risk of thallium pollution. For this reason the mobility of the element in soil and bottom sediment fractions and in surface water in those areas needs to be investigated. Flow-injection differential-pulse anodic stripping voltammetry (FI-DP-ASV) is an excellent tool for such investigation. FI-DP-ASV enables the thallium determination at concentrations of picomole per litre and medium exchange when the analysed soil or sediment fraction contains interferents.

The object of this work was to determine the mobility of thallium in soil and bottom sediments, as well as surface water, in an area of lead-zinc ore mining and processing near Olkusz (Poland). Several rivulets flowing in this area were

investigated in terms of thallium concentration in fractions of bottom sediments, flood-plain terraces and in surface water. Sequential extraction of soil was performed in accordance with the BCR procedure. The link between ore processing and thallium concentration is clearly observable. However, the major part of thallium is contained in the primary parent matter and is basically immovable.

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PP091

NEW MONITORING SUBSTANCES FOR THE INDIRECT TENSAMMETRIC TECHNIQUE

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The indirect tensammetric technique (ITT) is limited in application to the determination of non-ionic surfactants (NS). This technique has been developed in order to overcome problems with the very complex tensammetric behaviour of surfactant mixtures. The lowering of the monitoring substance peak due to competitive adsorption of the investigated surfactants is the analytical signal in ITT. Usually a saturated solution of ethyl acetate is used as the monitor. Despite the limited range of application, ITT is very useful because of the widespread use of NS, their common presence in the aquatic environment, and the lack of better methods. So far saturated ethyl acetate has proved to be the best monitor. It forms a single well-shaped tensammetric peak which reacts approximately additively for different NS. No problems with surfactant mixtures are observed. Ethyl acetate reacts only to NS, while anionic surfactants are highly tolerated. However, the disadvantage of this monitor is the technically difficult stage of dissolution of ethyl acetate. This is the crucial obstacle to the automation of the whole measurement cycle.

The aim of this work was to identify another monitoring substance having the same advantages as ethyl acetate, but with better solubility in the supporting electrolyte. The expected properties are the formation of a single well-shaped tensammetric peak located at approximately -1.25 V vs SCE, and satisfactory solubility in the supporting electrolyte. Among the substances subjected to preliminary testing, two display these properties: pentanol and iso-hexanol (4-methyl-2-pentanol). The solubility of both substances in a supporting electrolyte is much higher than for ethyl acetate, and their peaks are located within the expected range. Both tested monitors responded to different concentrations of a model NS (Triton X-100). Γ -shaped calibration curves were recorded. Tolerance to an anionic surfactant – dodecylbenzene sulphonate – was checked.

PP092**SIMULTANEOUSLY VOLTAMMETRIC DETERMINATION OF DOPAMINE AND ASCORBIC ACID AT PLATINUM ELECTRODE MODIFIED WITH PEDOT-PRUSSIAN BLUE HYBRID FILMS****STELIAN LUPU^a and PAUL CATALIN BALAURE**

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The analytical determination of dopamine (DA) has attracted a great deal of interest due to its physiological role as neurotransmitter¹. The electroanalysis of DA is hindered by the presence of other biologically active compounds, such as ascorbic acid (AA)². Therefore, selectivity and sensitivity are important in the development of new electrochemical sensors for DA quantification. The use of electrodes modified with inorganic redox mediator and/or conducting polymers is very promising³. In this work, the voltammetric determination of DA in presence of AA at platinum electrodes modified with poly-[3,4-ethylenedioxythiophene] (PEDOT) and Prussian Blue (PB) hybrid films is reported. The hybrid inorganic-organic coating has been prepared by a two steps method. Firstly, the PEDOT film was deposited onto electrode surface by potentiodynamic polymerisation in aqueous solution in the presence of ferricyanide ions. The obtained ferricyanide-doped polymer film was transferred in iron (III) ions containing aqueous solution, where the electrode potential was cycled from 0.6 to –0.4 V vs. SCE. During the potential cycling PB is formed inside the PEDOT matrix. The composite modified electrode was investigated in buffered aqueous solutions by using cyclic voltammetry and square wave voltammetry. The electrocatalytic activity of the composite coating towards the dopamine oxidation has been also investigated. The composite coating showed a high electrocatalytic effect towards the dopamine oxidation in the presence of ascorbic acid. A linear dependence of the anodic peak currents from square wave voltammetry over the dopamine concentration ranging from 5×10^{-5} to 6×10^{-4} M, in the presence of 1×10^{-2} M AA, was obtained. A detection limit (S/N = 3) of 2×10^{-5} M has been also obtained. The new modified electrode could be used as electrochemical sensor for simultaneous determination of dopamine in the presence of a high amount of ascorbic acid.

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PP093**ELECTROCHEMICAL DETECTION OF DOPAMINE AT PLATINUM ELECTRODE MODIFIED WITH INORGANIC-ORGANIC HYBRID MATERIALS****STELIAN LUPU^{a,*}, PAUL CATALIN BALAURE^b, CECILIA LETE^c, and MARIANA MARIN^c**

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The development of voltammetric sensors for the determination of dopamine has received a considerable interest during last few years. Dopamine (DA) is one of the important neurotransmitters widely distributed in the mammalian brain tissues¹. A major drawback in the quantification of DA is the presence of interfering compounds such as ascorbic acid (AA). Both these compounds show closely voltammetric peaks at unmodified electrodes. Therefore, the use of electrodes modified with different mediators can solve this problem².

In the present contribution, the voltammetric determination of DA at platinum electrodes modified with hybrid inorganic-organic coating consisting of poly-[3,4-ethylenedioxythiophene] (PEDOT) and Prussian Blue (PB) is reported. The modified electrode was prepared by electrochemical polymerization of EDOT in aqueous solution containing potassium ferricyanide. The obtained polymer modified electrode was immersed in aqueous solution containing iron (III) chloride and the electrode potential was scanned from 0.6 to (–0.2) V vs. SCE. During the potential cycling the PB is formed inside the PEDOT matrix. The hybrid inorganic-organic coating exhibits good electrocatalytic properties in dopamine oxidation. In square wave voltammetry a linear response was obtained in the range of 1×10^{-5} to 1×10^{-3} M.

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PP094**VALIDATION OF ELECTROANALYTICAL METHOD FOR DOPAMINE DETERMINATION IN THE PRESENCE OF INTERFERENTS****STELIAN LUPU* and ION ION**

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Many analytical methodologies, such as electrochemical, chromatographic, were established for the determination of dopamine (DA) in real samples¹⁻³. In this paper a voltammetric method for the determination of DA in presence of ascorbic acid (AA) at platinum electrodes modified with poly-[3,4-ethylenedioxythiophene] (PEDOT) and Prussian Blue (PB) hybrid films is reported. The hybrid films have been prepared by potentiodynamic polymerisation of EDOT in aqueous solution in the presence of ferricyanide ions, followed by potential cycling in iron (III) ions containing aqueous solution. By this procedure a hybrid PEDOT-PB coating is obtained. The hybrid coating exhibited good electrocatalytic effects towards DA and AA oxidation. A decrease of anodic peak potentials of about 200 mV in comparison with the unmodified electrode was obtained. The response of the electrochemical sensor towards DA was linear over the concentration range from 5×10^{-5} to 6×10^{-4} M, in the presence of 1×10^{-2} M AA. The detection limit (S/N=3) of 2×10^{-5} M has been obtained. The results obtained through this electroanalytical method were validated and compared to analytical data obtained by high liquid performance chromatography.

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PP095**STUDY OF BASE SEQUENCES IN OLIGODEOXY-NUCLEOTIDE NONAMERS BY ELECTRO-CHEMICAL AND CHROMATOGRAPHIC TECHNIQUES****SAMUEL MACH, MARTA FARKOVÁ, and LIBUŠE TRNKOVÁ***

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The structure of oligonucleotides (ODN's) corresponds to their properties and behavior in organisms. This work deals with the study of electrochemical and chromatographic behavior of ODN's in relation to sequences of nucleic acid bases in the ODN chain. Twenty ODN nonamers with different sequences of adenine (A) and cytosine (C) but with the same ratio of A:C (3:6) were investigated by high performance liquid chromatography (HPLC) with UV/Vis detection and by linear sweep voltammetry (LSV) and/or elimination voltammetry with linear scan (EVLS)¹⁻³. In electrochemical methods our interest was focused on the reduction signals of A and C measured at mercury electrode, in separation method on retention times of ODN. Both electrochemical and chromatographic data obtained were consequently evaluated by artificial neural network (ANN). We constructed ANN models using different inputs including selected points of LSV or EVLS curves (peak heights of separated reduction signals of A and C or differences of reduction A and C potentials from EVLS curves) and retention times from HPLC measurements. Moreover we used supplementary parameters such as extinction coefficients at 260 nm, melting points, ΔH and ΔS of the stacking effect⁵⁻⁶. The best results were obtained from the model with the following inputs: 50 points from LSV curve taken at reference scan rate 200 mV s^{-1} , retention times and all supplementary parameters.

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PP096**AMPEROMETRIC BIOSENSOR FOR DOPAMINE DETERMINATION BASED ON ELECTRO-DEPOSITION OF OVEROXIDIZED POLYPYRROLE ON SOL-GEL-DERIVED BIOSENSOR****MIR REZA MAJIDI*, KARIM ASADPOUR-ZEYNALI, and SIMA GHOLIZADEH**

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Conducting polymers such as polypyrrole, are being compared with the classical electrode materials such as metals and glassy carbon in electroanalytical applications and chemi-

cal sensors or biosensors¹. Polypyrrole undergoes overoxidation at more alkaline media, has been regarded which leads to the loss of conductivity and dedoping. Several reports on the use of sol-gel chemistry in the development of biosensors have received extensively in the past few years^{2–4}. Plant tissue containing the enzymes and these plants based biosensors offer a good alternative compared with biosensors based on isolated enzymes⁵. An amperometric biosensor based on overoxidized polypyrrole (OPPy) coated on sol-gel bioelectrode was developed by entrapment of plant tissue into sol-gel matrix. Polymer film was electrochemically synthesized by electrooxidation of 0.1 M pyrrole in aqueous solution onto the sol-gel biosensor. Amperometric measurements were performed at a constant potential of 0.4 V vs. SCE. The OPPy-modified sol-gel bioelectrode showed a high activity for the electrooxidation of dopamine (DA) at $E_p = 0.163$ V vs. SCE. The effects of pH, pyrrole concentration and potential range of polypyrrole overoxidation on the response of the electrode were elucidated. The modified bioelectrode presented a linear response range for DA from 9.99×10^{-6} M upto 1.1×10^{-3} M by amperometry. The diffusion coefficient of 6.86×10^{-8} for DA was also obtained using chronoamperometry study. The response of the overoxidized polypyrrole coated sol-gel electrode and uncoated sol-gel electrode were compared. The sensitivity and the stability of the biosensor were also determined. The biosensor was applied for the determination of dopamine in pharmaceutical formulations.

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PP097

MULTISENSOR ANALYSIS OF HOMOLOGOUS NON-IONIC SURFACTANTS

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Quantitative non-ionic surfactant determination is a complex analytical problem as various composite mixes, wastewaters, sewage sludges, etc. contain mixtures of their isomers, homologues and oligomers. For detection polyoxyethylated

alkylphenols and their degradation products in various objects different separation techniques with subsequent detection are used. To this end, spectrophotometry, solid-phase extraction with high-performance liquid chromatography and fluorescence, thin layer, gas chromatography, chromatography-mass spectrometry are most often employed. Lately, multi-sensor systems with multivariate calibration technique ("electronic tongue") have been employed for fast qualitative and quantitative analysis of multi-component solutions. The basic requirements to an array sensor are a low selectivity and a high cross-sensitivity.

Samples of polyoxyethylated nonylphenols

$C_9H_{19}C_6H_4O(C_2H_4O)_mH$ ($m = 10-100$) with a purity of 96–98 % were investigated. Compounds of polyoxyethylated nonylphenols with barium and tetraphenylborate ions (for example, nonylphenol-12-Ba-tetraphenylborate) were used as electrode-active compounds of membranes sensitive to non-ionic surfactants.

Low selectivity, high cross-sensitivity of surfactant sensor, and also identity of their electrochemical and transport parameters are a basis for designing multi-sensor systems for determination of homologous non-ionic surfactants in various objects (model mixtures, artificial polluted natural waters).

Analytical signals from non-ionic surfactant sensor arrays were processed by partial least-squares algorithm (PLS) and artificial neural networks (ANN) with back propagation of errors. At PLS processing the responses from surfactant sensor arrays were randomly parted into a set for training (to create a model) and a reference one for checking its forecasting capacity. To employ the artificial neural network technique the data were randomly splitted into calibration, monitoring and validation sets. Three-layered neural networks were used. The number of neurons in the input layer corresponded to the number of sensors in the array. The concentration of non-ionic surfactants, for example, in the three-component model mixture ranged from 1×10^{-5} to 2.2×10^{-3} mol l⁻¹ for nonylphenol-10, 1×10^{-5} – 2×10^{-3} mol l⁻¹ for nonylphenol-30, 1×10^{-5} – 3×10^{-3} mol l⁻¹ for nonylphenol-40 at different component ratios. The mean relative error of homologous non-ionic surfactant detection was 7 to 9 % for PLS and 3 to 4 % for ANN. The results of neural network training can be used for analysis both three-component model mixtures and two-component model mixtures.

The possibility of designing of surfactant sensor arrays for separate definition of homologous polyoxyethylated nonylphenols in two-, three-, four-component systems (model mixtures and artificial polluted natural waters) is shown. The least relative errors of detection were obtained for ANN.

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PP098**HIGHLY SENSITIVE DETERMINATION OF IODIDE BY ION CHROMATOGRAPHY WITH AMPEROMETRIC DETECTION AT A SILVER BASED CARBON PASTE ELECTRODE****TRESOR KIMBENI MALONGO^{a,b}, STEPHANIE PATRIS^a, PASCALE MACOURS^c, FREDERIC COTTON^{a,c}, J. NSANGU^b, and JEAN-MICHEL KAUFFMANN^{a*}**

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A silver based carbon paste electrode was developed for use as detector in ion chromatography (IC) for the sensitive determination of iodide in real samples. Micro and nanoparticles of silver were investigated for different electrodes fabrication.

The iodide assay was based on ion chromatography with amperometric detection (IC-AD) at a silver composite electrode polarized at +0.080 V versus Ag/AgCl. Free iodide and organoiodide compounds were studied. The detection process was characterized by studying the redox behavior of iodide ions at both silver and silver composite electrodes by cyclic voltammetry. The presence of iodide ions in solution was found to considerably facilitate metallic silver oxidation, with response currents directly related to iodide concentration. The calibration curve at the selected silver composite electrode was linear in the concentration range comprised between 0.635–63.5 $\mu\text{g L}^{-1}$ iodide. The relative standard deviation (RSD) for successive injections was below 3 % for all iodide standard solutions investigated. The limit of detection (LOD) was 0.47 $\mu\text{g L}^{-1}$ (3.7 nmol L⁻¹) for an injection volume of 20 μL , i.e. 74 fmol injected. The IC-AD method was successfully applied to the determination of iodide in complex real samples such as table salts, sea products and iodide bound drug compounds. The analytical accuracy was verified by the assay of iodide in milk powder from a iodide Certified Reference Material (CRM) BCR 150.

PP099**USE OF BISMUTH FILM ELECTRODE FOR THE CATHODIC ELECTROCHEMICAL DETERMINATION OF TRIAZINE HERBICIDES****MÓNICA MORENO^a, ESPERANZA BERMEJO^a, MANUEL CHICHARRO^a, ALBERTO SÁNCHEZ^a, and ANTONIO ZAPARDIEL^b**

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Since its introduction in stripping analysis¹, the bismuth film electrode (BiFE) has been accepted in many electroanalytical laboratories worldwide. BiFEs have found a wide range of application in anodic stripping voltammetry, potentiometric stripping analysis as well as in cathodic adsorptive stripping voltammetry for the determination of some metals. On the other hand, its application for the determination of organic compounds has been much less studied².

In this communication, a square wave cathodic voltammetry (SWCV) procedure for herbicides determination at an *ex situ* plated BiFE is described. Different herbicides with reductive moieties, emphasizing in the triazine derivatives, were subjected to study. Carbon-based substrates have been studied for the preparation of *ex situ* bismuth film electrodes as well as the influence of relevant parameters upon the bismuth film formation (plating solution, deposition potential and deposition time).

The use of bismuth film electrode present advantages over the plain substrate electrodes such as low reduction overpotential and good stability for the electroanalysis of herbicides in acidic media even in the presence of oxygen and could be a good alternative to the toxic mercury-based electrodes.

The authors wish to thank Ministerio de Educación y Ciencia de España (Project CTQ 2004-06334-C02-01-02), Universidad Autónoma de Madrid and Comunidad Autónoma de Madrid (Projects: CCG06-UAM/SEM-0124 and CCG07-UAM/SEM-1752).

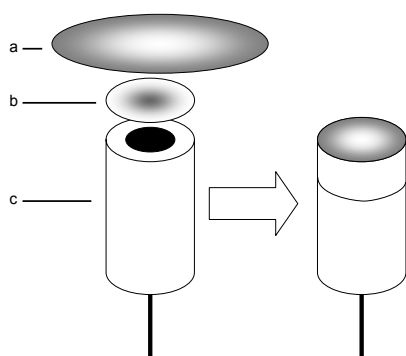
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PP100**SENSOR BASED ON ELECTROSPUN NYLON NANOFIBERS****SAVERIO MANNINO^{*}, MATTEO SCAMPICCHIO, and NATHAN S. LAWRENCE**

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A web-like membrane consisting of nylon nanofibers, prepared by electrospinning, was used to produce an electrochemical biosensor for the sensible sensing of glucose¹. Glucose oxidase was immobilized (1) by physical adsorption on the platinum electrode surface, (2) by physical adsorption through the nylon net, and (3) by chemical bonding between the enzyme and the membrane, with glutaraldehyde as a cross-linker. In all the three set-ups, the advantages arisen by use of the nylon net were evident. The nylon nanofiber net exhibits an high surface to volume ratio compared with the usual thick nylon support. This allows unique chemical features that can be summarized as: (a) excellent support properties which prevent leakage of the enzyme; (b) selective physisorption of



Scheme 1. Example a possible electrode assembly a) electrospun nanofiber b) layer of glucose oxidase immobilized by drop coating c) working electrode

interferents (such as polyphenols) by changing the protonation of nylon amine group, (c) prevention of the electrode passivation, (d) enhanced biosensors' longevity. The advantages of the new nanofibers strip-coated biosensor will be discussed via the electrochemical sensing of glucose in real food matrices.

We thank Cariplo's Foundation.

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PP101

MICROCONTROLLER-BASED POTENTIOSTAT DEVELOPED USING THE LTCC TECHNOLOGY

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The miniaturization of amperometric chemical analyzers involves the dimensional reduction of electrodes to the micrometer scale. To generate stable potentials and to obtain precise measurements, high-sensitivity electronic circuits are required. The low temperature cofired ceramics (LTCC) technology has been widely applied to the production of multilayer printed circuit boards due to its excellent electrical, mechanical and thermal properties^{1,2}. Its compatibility with serigraphic techniques and its fabrication process enable the aggregation of several layers to obtain multilayer circuits, which results in high-density boards of elevated complexity and small size. In this work, the development of a microcontroller-based potentiostat using LTCC technology is presented (see figure 1). Since the potentiostat is based on a microcontroller, several amperometric techniques can be applied (cyclic voltammetry, differential pulse voltammetry, square-

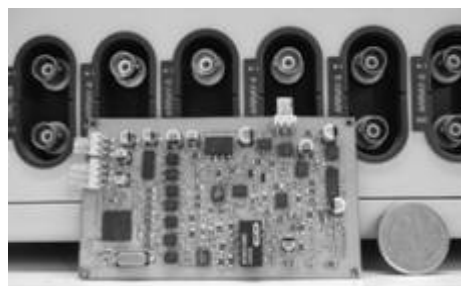


Fig. 1. Microcontroller-based LTCC potentiostat

wave voltammetry, etc.). The instrument was designed to work in four current ranges to improve sensitivity at different intensity levels. Results showed a high signal to noise ratio with a base line of ± 0.5 nA, comparable with commercial instruments.

Since the LTCC technology permits the fabrication of complex three-dimensional structures, microfluidic systems can be easily developed and integrated with electronics to obtain real micro total analysis systems (μ TAS).

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PP102

GENOSENSOR FOR SARS VIRUS DETECTION BASED ON GOLD NANOSTRUCTURED SCREEN-PRINTED CARBON ELECTRODES

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The present work describes the design of a genosensor for a sequence of the SARS virus using gold nanostructured screen-printed carbon electrodes (SPCEs) as transducers.

SPCEs are *in-situ* modified with gold in order to get nanostructured surfaces by applying a constant current intensity of $-5 \mu\text{A}$ for 2 minutes using a 0.1 mM AuCl_4^- acidic solution. The nanostructured obtained following this methodology is showed in Fig. 1.

The design of the genosensor consists on the immobilization of thiolated probe strands over the surface, and after a blocking step, hybridization with biotin labeled target strands is carried out. Then, streptavidin labeled with alkaline phosphatase is used to catalyze an enzymatic reaction that leads to the analytical signal; an electrochemical process of silver¹.

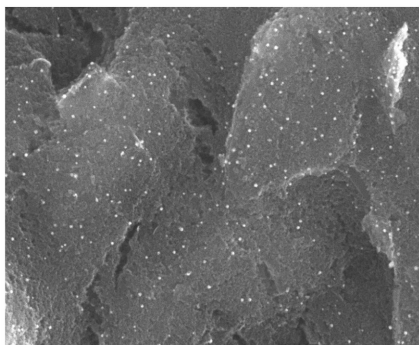


Fig. 1. SEM image of the gold nanostructure used as transducer

Following this methodology, SARS virus targets can be determined in a quantitative range from 5 pM to 100 pM. The use of these gold nanostructured surfaces improves the sensitivity obtained with continuous gold surfaces² with less consumption of reagents.

This work has been supported by Spanish Project: BIO2006-15336-C04-01.

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PP103

SOFT-LANDED PROTEIN VOLTAMMETRY FOR REDOX PROTEIN CHARACTERIZATION

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Microperoxidase-11 (MP-11) was soft landed onto the gold surface of a screen printed electrode. Intact protein deposition was verified by time of flight secondary ion mass spectrometry (ToF-SIMS). The coupling of soft landing with electrochemical techniques allowed unique information to be obtained about the deposition features. A full characterization of the direct electron transfer properties was performed by modeling data obtained from cyclic voltammetry experiments; calculated values of kinetic electron transfer constant, formal redox potential allow us to hypothesize the mechanism involved in soft landing immobilization and demonstrate the different conformation of the enzyme deposited from two

different charged species. The strong interaction between MP-11 and the gold surface and long-term stability of the functionalized electrode characterize the peculiar features of this procedure which enhance its power with respect to the existing immobilization procedure and ensure its suitability for those practical applications which could benefit from an unmediated bridgeless bioelectrochemical electron transfer.

This project has been co-funded by the European Commission under contract number 017350 (BioMedNano).

PP104

As(III) QUANTIFICATION BY SQUARE WAVE ANODIC STRIPPING VOLTAMMETRY AT A PLANAR SILVER ELECTRODE

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Arsenic is a toxic element which is known to be carcinogenic. Arsenic is found in a wide variety of chemical species throughout the environment and can be readily transformed by microorganisms, changes in geochemical conditions, and other environmental processes. While arsenic occurs naturally, it can be found as consequence of a variety of industrial applications, including leather and wood treatments, and pesticides.

Based on the fact that water consumption is the most important source for Arsenic poisoning, the World Health Organization has established 10 mg L⁻¹ as the provisional concentration guideline for total arsenic concentration in drinking water. Nevertheless, in many countries this concentration has been overcome, which is found to be related with adverse effects to population health¹.

Looking for a simple, affordable, sensitive and easy-to-implement quantification alternative for *in-situ* analysis of arsenic, diverse electrochemical methods based on anodic stripping voltammetry (ASV) have been recently reported. In spite of the great advantages of arsenic analysis by ASV, some disadvantages are distinguished, like the toxicity or the expensive cost of working electrodes (Hg, Au and Pt)².

In the present study an electrochemical assay for As(III) quantification using square wave anodic stripping voltammetry at silver screen-printed electrodes is presented. The planar strips demonstrate a good behavior even without stirring the plating solution during the deposition process and in presence of dissolved oxygen. The detection limit was 10 µg L⁻¹ and the linearity range from 19 to 300 µg L⁻¹. The effect of the most important ion interferences (Cl⁻, Hg²⁺, Pb²⁺ and Cu²⁺) on stripped signal is also described. The proposed electrodes demonstrated to be suitable for *in-situ* As(III) analysis.

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PP105

DETERMINATION OF GUANOSINE 5'-MONOPHOSPHATE BY SQUARE WAVE VOLTAMMETRY WITH A MODIFIED GOLD ELECTRODE

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The aim of the present work was the study of electrochemical behaviour and the subsequent determination of the nucleotide guanosine 5'-monophosphate (GMP) by square wave voltammetry (SW). For these studies a modified gold electrode was used. First, a modification with an organosulphur compound was made, 1,2-ethanedithiol (EDT), which acted as a spacer and it spontaneously bonded to the surface of gold electrode (Au-EDT). Then, the electroactive surface of electrode was increased with gold nanoparticles (AuNPs), producing a spontaneous chemistry adsorption with the sulphur compound (Au-EDT-AuNPs). The formation and characterization of the nanoparticles solution were realized by UV-VIS spectroscopy and an Atomic Force Microscopic (AFM). The complementary nucleotide of GMP with an atom of sulphur in its structure (4-amino-2-mercaptopyrimidine, TC) was utilized for the detection and quantification of GMP; a spontaneous bond between complementary nucleotide and gold nanoparticles was formed, and the modification of gold electrode was finished. For successive studies the totally modified gold electrode was used and was denoted as Au-EDT-AuNPs-TC.

When the modification of electrode was optimized, the electrochemistry study and optimization of the conditions of measurement were realized for the direct determination of GMP by square wave voltammetry.

The authors thank the Spanish Education Ministry for financial support (Project CTQ2004-04142/BQU) and a grant scholarship to Laura Mora (AP2005-0266).

PP106

H₂O₂ DETERMINATION AT IRON-RICH CLAY MODIFIED ELECTRODES

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Clay modified electrodes (CME) have been studied extensively because of the ion exchange properties of the clays, their layered structure and their chemical stability. The major constituents of most common smectite clays are aluminum and magnesium. But natural clays are never pure, they always contain small amount of other elements, i.e. iron. These trace elements can affect the response of CME with an electrocatalytic behavior. For instance, Oyama and Anson reported that structural iron sites could mediate the reduction of hydrogen peroxide¹. However the proposed redox activity of iron in CME has always involved adsorbed electroactive species as charge mediators (Ru(NH₃)₆²⁺, Fe(bpy)₃³⁺, MV²⁺)²⁻³. Electroluminescence experiments confirmed that iron species contained in the clays can mediate an electron transfer^{4,5}.

In this study, we investigated the electrochemical properties of several ferruginous clays, either natural or synthetic. Three different conditions have been tested at the CME for the reduction of H₂O₂:

- a) in acidic medium without redox mediator,
- b) in neutral medium (pH 8) with adsorbed MV²⁺ as a charge shuttle,
- c) in neutral medium (pH 7) with adsorbed Hemoglobin as a biocatalyst.

The resulting CME were characterized by cyclic voltammetry in the presence or not of H₂O₂ and finally the calibration curves were recorded under amperometric conditions. The results will be discussed in relation to the clay properties, in particular the iron amount present in their structure and its structural sites.

This work is supported by the CMCU (06/S1207) et MIRA 2007.

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PP107

VOLTAMMETRIC DETERMINATION OF 2,4-DINITROPHENOL AT BORON-DOPED DIAMOND FILM ELECTRODE**JANA MUSILOVÁ^a, JIŘÍ BAREK^{a*}, PAVEL DRAŠAR^b, and KAROLINA PECKOVÁ^a**

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Boron doped diamond (BDD) is a novel and versatile electrode material, which has gained popularity in a variety of electrochemical applications^{1,2}. BDD thin-film electrodes possess excellent electrochemical properties, such as extreme hardness, low and stable background current over a wide potential range, microstructural stability at extreme cathodic and anodic potentials, high current densities, good responsiveness for many redox analytes without pretreatment, and resistance to electrode fouling³.

Nitrophenols coming from pesticide degradation, car exhausts, and industrial wastes are listed as priority pollutants by the US Environmental Protection Agency. They are considered to be potentially carcinogenic and mutagenic. Pesticides based on simple nitrophenols are used as growth stimulators in agriculture⁴. Moreover, 2,4-dinitrophenol (2,4-DNP) is a suitable model of nitrated explosives⁵. 2,4-DNP has been determined at BDD film electrode (Windsor Scientific, UK) by differential pulse voltammetry. The influence of pH at voltammetric behavior of 2,4-DNP was investigated using electrochemical reduction and oxidation in Britton-Robinson buffer over a pH range of 2–12. The concentration dependences were measured under optimum conditions. The voltammetric behavior of 2,4-DNP has been compared with 2-nitrophenol and 4-nitrophenol.

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PP108

POLYMER – IONIC LIQUID ELECTROLYTES FOR ELECTROCHEMICAL GAS SENSORS**MARTINA NÁDHERNÁ^{a,b}, FRANTIŠEK OPEKAR^b, and JAKUB REITER^{a*}**

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Room temperature ionic liquids attract the attention thanks to their excellent properties: non-volatility, high conductivity, liquidity in wide temperature range, high thermal stability (up to 400 °C) and low toxicity¹. Especially for electrochemical gas sensors their high electrochemical stability is highly appreciated².

Our recent research is aimed at development of new binary systems polymer-ionic liquid serving as an electrolyte for electrochemical gas sensor for NO₂. Previously used electrolytes were usually ternary systems polymer-aprotic solvent-salt^{3,4}, while now is the function of embedded solution of salt in a solvent substituted with a hydrophobic ionic liquid based on 1-methylimidazole. We have combined several ionic liquids with various methacrylate polymers forming elastic, homogenous and long-term stable electrolytes.

Experimental

Following monomers or macromonomers (2-hydroxyethyl methacrylate HEMA, poly(ethylene glycol) methacrylate PEGMA and poly(ethylene glycol) methyl ether methacrylate PEGMEMA – all from Sigma-Aldrich) and ionic liquids (1-butyl-3-methylimidazolium hexafluorophosphate BMIPF₆, 1-butyl-3-methylimidazolium tetrafluoroborate BMIBF₄ and 1-ethyl-3-methylimidazolium tetrafluoroborate EMIBF₄ – all prepared following literature^{1,5,6}) were combined.

Polymer electrolytes were prepared by direct, thermally initiated radical polymerization (150 min at 80 °C) of the initial liquid mixture containing the monomer, ionic liquid and polymerization initiator (2,2'-azobis(isobutyronitrile)). The polymerization was carried out in a cell formed of polypropylene plate, packing distance frame (silicone rubber) and glass plate.

Electrochemical characterization of prepared electrolytes was performed on a potentiogalvanostat PGSTAT 30 (Eco Chemie, The Netherlands) including the FRA-2 module for impedance measurements.

Results and discussion

The first objective was to find chemically compatible pair of a monomer and a strongly polar ionic liquid. Therefore more polar monomers containing either -OH group and/or (CH₂CH₂O)_n units in the structure were employed.

The combinations PEGMEMA-BMIPF₆ and PHEMA-BMIBF₄ form samples with suitable mechanical properties allowing both manipulation and electrochemical tests such as impedance and voltammetrical measurements.

Impedance measurements showed a reasonable ionic

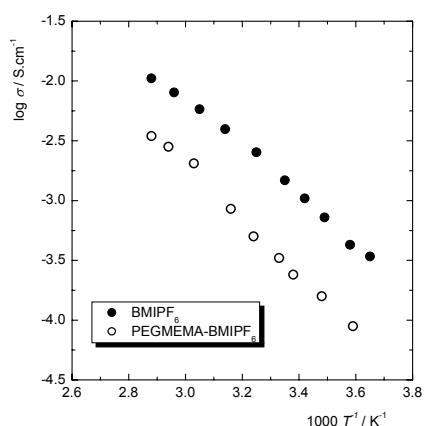


Fig. 1. Dependency of conductivity on reciprocal temperature of PEGMEMA-BMIPF₆ electrolyte (43:57 mol.%) and neat BMIPF₆

conductivity of PEGMEMA-BMIPF₆ electrolyte (2.4×10^{-4} S cm⁻¹ at 20 °C). Fig. 1 shows the relationship between conductivity and temperature of a polymer electrolyte and neat ionic liquid.

Voltammetrical measurements on a platinum electrode showed a broad accessible electrochemical window, especially in the case of electrolytes with PEGMEMA polymer. The absence of a hydroxyl group ensures the electrochemical stability from -2.3 to 2.5 V vs. Cd-Cd²⁺ making the electrolytes perspective also for lithium-ion batteries.

Subsequently, the electrolytes characterized above will be tested in an electrochemical sensor designed in previous research^{3,4}.

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PP109

ONE-STEP ENCAPSULATION OF BIOMOLECULES IN ELECTROGENERATED SOL-GEL FILMS FOR BIOSENSING APPLICATIONS

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Sol-gel electrochemistry has gained great popularity in the past decade, mostly because of the ease of formation of silica and organo-silica films with tailor-made properties that can be advantageously exploited for several applications when coated on a suitable electrode surface¹. The usual way to get such films involves either dip- or spin-coating a sol-gel medium containing the appropriate (organo)alkoxysilane precursor(s), which are hydrolyzed and (co)condensed on the electrode surface. Such film-modified electrodes have found applications in various fields including electroanalysis and sensors, electrocatalysis, or bioelectrochemistry¹.

Some years ago, Shacham and co-workers have developed a new and elegant electrochemically-driven deposition method for getting sol-gel thin films on conducting substrates². The approach is based on altering the surface pH by applying a suitable potential to an electrode immersed in a sol-gel medium, inducing thereby the catalysis of the condensation process thus enhancing the rate of film deposition^{3,4}.

This work points out that electrogeneration of silica gel films on glassy carbon electrodes can be applied to immobilize biomolecules – hemoglobin (Hb) or glucose oxidase (GOD) or both of them in mixture – without preventing their activity. These proteins were physically entrapped in the sol-gel material in the course of the electro-assisted deposition process applied to form the thin films onto the electrode surface. Successful immobilization of proteins was checked by various physicochemical techniques. Hb entrapped in the silica thin film displayed an electrocatalytic behavior towards O₂ and H₂O₂ in solution, respectively in the mM and μM concentration ranges. Immobilized GOD kept its biocatalytic properties towards glucose. Combined use of these two proteins in mixture has proven to be promising for detection of glucose in solution via the electrochemical monitoring of oxygen consumption (decrease of the oxygen electrocatalytic signal)⁵.

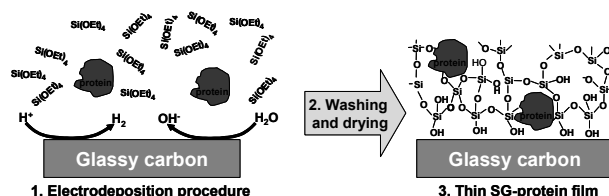


Fig. 1. Electrogeneration of sol-gel films in the presence of proteins

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PP110

THE DETERMINATION OF DIFFUSION COEFFICIENT OF MONOSACCHARIDS WITH ELECTROCHEMICAL MICROSCOPY

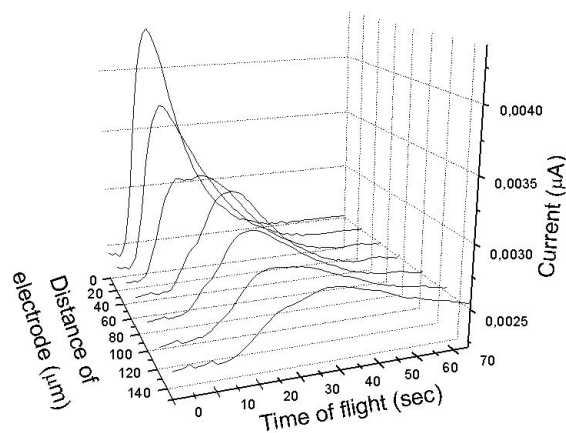
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The diffusion coefficient of carbohydrates in different media is an important parameter in several areas. High numbers of methods are available for measuring it. Several of them use electrochemical detection.

A simple method, based on special capability of Scanning Electrochemical Microscopy (SECM) for the accurate measurement of diffusion coefficient has been worked out in our laboratory.

It is based on detecting the concentration – time transients with appropriate electrochemical micro-sensor positioned at the close vicinity of a miniature dose source device. At given time (t_i) a small dose of the investigated species is introduced. The $\Delta t_{\max} = (t_{\text{cmax}} - t_i)$ value and the distance ($d = x + \Delta x_n$) between the source and the detector microelectrode are used for calculation of D . While the original set distance (x) can not be accurately measured in the micrometer scale, the tip travel distance (Δx_n) of the microscope is well defined. Collecting a few $\Delta t_{\max} - (x + \Delta x_n)$ data pairs reliable value of the diffusion coefficient can be obtained. The procedure is



simple and does not require knowing the dose size introduced.

In the work, to be presented the basic principle of the new method will be presented, and the values obtained with it will be compared with diffusion coefficient values obtained using conventional electrochemical methods. In the experiments micro size copper SECM tip, enzyme sensor, and conventional size electrodes were used. Diffusion coefficients of glucose arabinose and other monosaccharide were measured.

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PP111

BIOSENSORS AND ELECTROCHEMICAL DETECTION TECHNIQUES FOR CLINICAL DIAGNOSIS

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Recently a new measuring method has been worked out in our laboratory. The so called periodically interrupted amperometry (PIA) was proved very useful in lowering the detection limit of membrane coated electrodes, like amperometric biosensors.

As it is well known, the amperometric enzyme electrodes are made of a voltammetric base sensing element and different layers -among them enzyme containing reaction layer- coating its surface. In conventional amperometry the electrode potential kept constant, and the current generated by the electrode reaction is detected.

The concentration of electroactive species formed in the enzyme catalysed reaction is decreased by the continuous action of the electrode process. In this way the stationer layer at the surface of the sensing element gets more or less depleted.

It was expected, that periodic interruption of the electrolysis, would allow time for reloading the layer at the close vicinity of the sensing element. This could result in higher current and lower detection limit in case of an enzyme sensor.

In our presentation the basic principle of the PIA method will be introduced. In the experimental work to be presented glucose and putrescine measuring enzyme electrodes were prepared with three different stationary layers on their surface.

Platinum disc electrodes were used for preparation of the enzymatic working electrodes. PIA measuring program was applied and optimized, selecting the optimal measuring (t_M) and resting (t_R) time periods and the data collecting parameters.

Conventional amperometric detection and PIA detection were compared. The signals obtained with the optimized PIA program was much higher than the current obtained with the

classical amperometry. Results show that the PIA detection extends the measurement range of membrane coated amperometric sensors. In clinical samples putrescine is in lower μM range. Therefore lowering the detection limit is an important step forward.

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PP112

CARBON PASTE ELECTRODE MODIFIED WITH COAL

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The electrochemical properties of coals have been mostly studied by means of measurement in the coal slurries in electrolytes¹. Carbon paste electrode modified with carbonaceous materials (eg. activated carbon) has been also used for this purpose².

Carbon paste electrode (CPE) with mixed coal was prepared in order to find another possibility to investigate coals or carbonaceous materials. Samples of the used bituminous coal were from Ostrava-Karvina Coal Mines District. They were already characterized by proximate, ultimate as well as micropetrographic analyses.

The electrode was prepared by procedure similar to preparation of clay modified CPE³. The prepared electrodes were tested as to their mechanical properties and potential range in various electrolytes (acetate buffer pH 3,6, HCl, KCl, and NaOH (all 0,1 mol l⁻¹)). The potential ranges of the coal modified electrodes were broader in all the tested electrolytes in comparison with the unmodified CPE, especially in the positive potential direction. Cyclic voltammetry of ion pair [Fe(CN)₆]^{3-/4-} exhibited low current values. An influence of coal particle size on the electrochemical behaviour of the coal CPEs was studied, too.

Deposition of Hg film on the surface of the coal CPE showed possibility to use it either as a substrate for metals deposition or as a means for study of the sorption properties of coals.

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PP113

COMPOSITE BIOELECTRODES BASED ON LIPIDIC CUBIC PHASE WITH CARBON NANOTUBE NETWORK

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The important features of biofuel cell are the ability to convert chemical energy to electricity with high efficiency, at room temperatures and under conditions close to physiological. Monoolein liquid-crystalline films is a convenient matrix to immobilize biocatalysts at the electrode surfaces in their active form. The lipidic cubic phase can be characterised as a curved, non-intersecting bilayer with two unconnected water channels. Monoolein (MO) is an example of a lipid forming such a phase. It is highly viscous, transparent and at hydration over 20 % is stable in contact with water. Doping MO with 1,2-dioleoyl-sn-glycero-3-phosphate increases the shear strength of the MO/H₂O cubic phase and makes the aqueous channels walls anionic allowing for more stable immobilization of cationic mediators inside the cubic phase due to electrostatic interactions. Using the monoolein cubic phase for hosting the enzymes allowed also to avoid any additional separating membranes in the biofuel cell, keeps the enzymes active and close to the electrode surface. In our membraneless biofuel cell (BFC) glucose oxidase and laccase were the anodic and cathodic catalyst, respectively, the bioanode was glassy carbon rod modified with the cubic phase containing glucose oxidase isolated from *Aspergillus niger* and tetrathiafulvalene (TTF), methylene green or ferrocenecarboxylic acid as the mediators. The biocathode was glassy carbon modified with the cubic phase and laccase from *Cerrena unicolor*. ABTS as the mediator was applied to this system. Such biofuel cell uses glucose as the anode fuel and dioxygen as the cathode fuel. We determined the main parameters of the presented biofuel cell. The open circuit potential V using TTF and ABTS mediators. was 450 mV The load in the range of 10 kΩ to 10 MΩ was applied to determine the cell current (*I*_{cell}) and the cell voltage (*V*_{cell}). The maximum power density was 7 μW cm⁻². To eliminate leaching of the mediators to the solution and improve current and power densities of the cell, selected mediators were bound covalently or adsorbed on single walled carbon nanotubes (SWNTs) forming a conductive network in the cubic phase film.

PP114

NOVEL TYPE OF SILVER AMALGAM PASTE ELECTRODE

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A new arrangement of silver amalgam paste electrode¹ (AgAPE) was developed for the voltammetric determination of 4-nitrophenol (4-NP). Due to easy surface renovation by simple procedure, the electrode was found to be useful for the determination of nitrated phenolic compounds in waste water. The electrode showed good reproducible results for 4-NP with relative standard deviation (RSD) 2.1 %. The reproducibility was also found good both in drinking water and river water with RSD 3.4 % and 4.8 %, respectively, without employing regeneration potential. The effect of electrode regeneration on peak current height was studied. The regeneration of electrode improved peak current stability with RSD 1.1 %. Under the optimized regeneration potential the peak current stability improved for 4-NP in drinking water but in river water it deteriorated which may be due to the presence of some other interfering substances. Some passivation has been observed for 2-methyl-4,6-dinitrophenol indicating that the passivation is connected with the properties of compounds. Furthermore, fairly good reproducibility (RSD lower than 10 %) of surface renovation has been observed. Under optimized condition the reduction peak currents were linear with the concentration of 4-NP from 4×10^{-7} to 1×10^{-4} mol L⁻¹ with the correlation coefficient of $R = 0.9997$. The limit of determination for 4-NP at AgAPE was 3×10^{-7} mol L⁻¹. The determination of 4-NP at AgAPE was carried out in model samples of drinking and river water and the limit of determinations were 2×10^{-6} and 3×10^{-6} mol L⁻¹, respectively.

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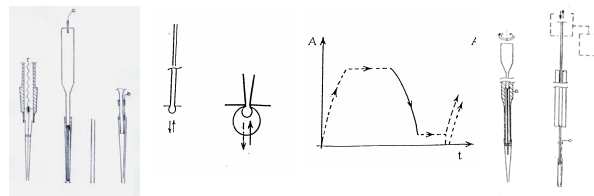
PP115

NEW TYPES OF MINIATURIZED (MINI- TO NANO-VOLUME) ELECTRODES, CAPILLARY OR PLASTIC-TIP SENSORS AND PORTABLE SYSTEMS, BASED ON MERCURY, AMALGAMS, COMPOSITE OR PASTE AMALGAMS, ETC

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Sensors/electrodes based⁵⁻⁹ on mercury, amalgams, solid or mercury modified amalgams, etc., occupy an important position among the working electrodes as to trace analysis¹⁻³ and study of bioactive species⁴. Recent development⁵⁻⁹ of the mentioned stationary, renewed stationary or (time-dependent) controlled-size electrodes has brought suggestion of numerous new types of useful designs and applications concerning, e.g., the miniaturized electromechanically renewed hanging (stationary) mercury drop HMDE/SMDE electrodes^{5,9}, meniscus or hemisphere sensors, compressible/expansible electrodes^{5,9}, the sensors based on the mercury modified solid amalgams⁷⁻⁹, composite or paste amalgams⁶ and materials of the analogous consistence, capillary, plastic-tip⁶, glass-tip⁶ and other sensors as well as portable (or mobile) measuring systems⁵. New regimes, modes and applications based on analysis of physico-chemical factors and functioning conditions have been suggested. Now even the mini-, semimicro-, micro- or nanovolumes (nanoliters)⁶ of the electrode phase can be used.



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PP116

NEW ELECTROANALYTICAL AND PHYSICO-CHEMICAL ASPECTS OF ELECTROCHEMICALLY RENEWED SENSORS BASED ON MERCURY OR AMALGAMS

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Use of purely mechanical renewal of the above-mentioned sensors (electrodes)^{1–6} based on mercury or amalgams results in adequate consumption of the electrode phase, depending on the applied experimental conditions. The ways how to reduce a consumption of mercury or amalgams have been explored and tested. The obtained results outlined, that a combination of the mechanical and purely electrochemical renewal of the electrode surface of HMDE seems to be useful for many electroanalytical as well as physico-chemical applications. This finding is supported by the adequate physico-chemical reasons and interpretation of corresponding interfacial behavior of species present in the measured solution.

For example, application of purely electrochemically pretreated HMDE produced analogous sharp cathodic DPV-peaks of 2-aminoanthraquinone 2-AA in 0.05 M BrRo:MeOH 1:1, pH 4.6 at the same depolarization potentials as in the case of application of mechanically renewed HMDE resulting in ΔV vs. c dependence of a parabolic shape exhibiting a more flat course approaching the linear dependence. It is so probably due to a time-dependent competition between adsorption of 2-AA and other multi-partial electrosorption interactions in the electrode boundary. There is a mixture of present physico-chemical (interfacial) processes influencing the actual state of the electrode surface. A reasonable sensitivity and reproducibility outlined a good analytical^{1–6}, biophysical⁷, etc., applicability of the discussed electrochemical renewal.

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PP117

GRAPHITE FOILS AS WORKING ELECTRODE SOURCE IN AMPEROMETRIC FLOW INJECTION ANALYSIS OF PHARMACEUTICAL MOLECULES

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Graphite foils are widely used as a sealing material for high temperature, high-pressure transfer of liquids, gases, steam, chemicals and corrosives, as gaskets material in automotive, petroleum, chemical, paper, and nuclear industries, and as bipolar plates in the fuel cell industry.

A potential application almost unexplored of bare graphite foil is the development of electrochemical sensors, aiming analytical applications. Graphite foils were used as substrate for enzyme immobilization for the confection of biosensors¹, as electrode for fuel cell^{2,3}, and as substrate to grow carbon nanotubes⁴.

Herein we describe the use of graphite foils as the working electrode in flow systems employing amperometric detection. In our studies, graphite foils were adapted in a flow cell and applied for the determination of pharmaceutical products.

Fig. 1 shows the electrochemical flow cell: It is constituted by two acrylic blocks (A), which are tighten by two screws (B). A polyethylene foil (C) containing a hole (G), which is positioned between the two blocks, over the graphite foil (D), used as working electrode. In the outlet channel of the cell, a stainless steel tube (E) works as the auxiliary electrode. Near to this tube, in the outgoing channel was positioned the miniaturized Ag/AgCl electrode (F). The arrows indicate the inlet and outlet of the solution. Polyethylene tubes are used to conduct the solution to the cell.

Prior to the electrochemical flow cell, there is an injection valve at which a sample loop with a fixed volume is injected in the flow system. The solution was propelled by the gravity force by placing a vessel containing electrolyte at 1 meter height and controlling the flow rate pinching a Tygon[®] tube which was inserted in the line.

Cyclic voltammetry was employed to investigate the

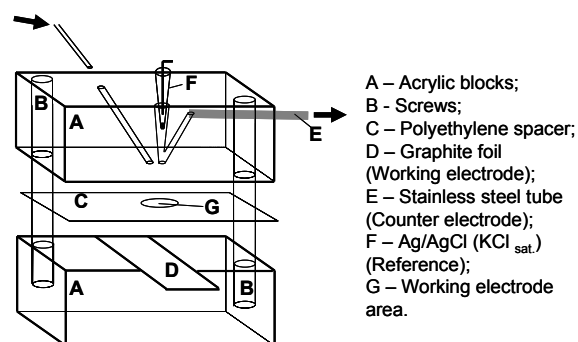


Fig. 1. Electrochemical cell for flow injection analysis (FIA) constructed in our laboratory. The arrows indicate the inlet and outlet of the carrier solution

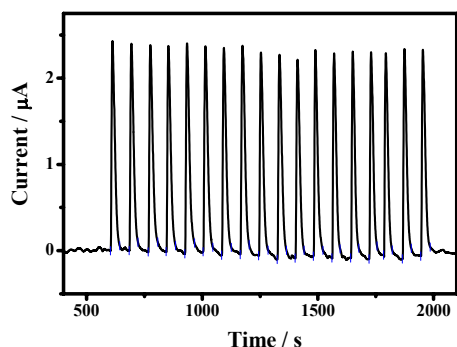


Fig. 2. Amperometric responses for eighteen consecutive injections of $1 \times 10^{-4} \text{ mol L}^{-1}$ acetaminophen

electrochemical oxidation of acetaminophen and ambroxol at graphite foil electrodes. The good performance for the alternative electrode allowed the use of amperometry in a FIA system. The first experiments were carried out to optimize the FIA system for the amperometric determination of acetaminophen.

The best conditions were +0.7 V as the working potential, flow rate of 2 mL min^{-1} , sample loop of $200 \mu\text{L}$, and $0.1 \text{ mol L}^{-1} \text{ KCl}$ as the supporting electrolyte. Fig. 2 shows the amperometric responses for eighteen consecutive injections of $1 \times 10^{-4} \text{ mol L}^{-1}$ acetaminophen under the optimized conditions. The relative standard deviation was 2.7 %.

These preliminary results show the potential application of graphite foils as electrochemical sensors for FIA systems. The advantages of using such material as electrode are its low cost, which would allow the production of disposable electrodes. The determination of ambroxol using the proposed analytical system is now been optimized. Graphite foil electrode may also be used as a substrate for electrodeposited catalysts to produce sensors with improved selectivity and sensibility.

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PP118

STUDY OF THE ELECTROCHEMICAL PROPERTIES OF RIGID COMPOSITES ELECTRODES AS A FUNCTION OF THEIR MWNT CONTENT

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Carbon nanotubes (CNT) have been attracting considerable attentions over the last decade due to their remarkable mechanical and electrical properties¹. CNTs have a novel structure, highly accessible surface area, low resistance, and high stability. It has been experimentally shown that composites based on the combination of CNT with a insulating matrix improve the electric conductivity as well as the mechanical properties of the original polymeric matrix^{2,3}. The transition from an insulating to a conducting composite is a function of the CNT loading. When a first network is developed throughout the insulating matrix, the composite resistivity lowers by several orders of magnitude. When this drop occurs, it is called percolation threshold. Although the variation of the mechanical and electrical properties of composite containing different CNT percentages, has been investigated and evaluated by other authors^{4,5}, their influence in the electrochemical properties of composites has not received the same attention..

The aim of the present study is to optimise the CNTs loading in the insulating matrix (resin epoxy) by means of electrical and morphological measurements and then to determine how the electrical properties affect the analytical response of the composites when they are used as amperometric sensors.

The multiwall carbon nanotubes used in this study (MWNT, purity > 95 %, length 5–15 μm , OD 10–30 nm) were supplied by SES Research (USA). The polymer matrix consisted of Epotek H77 with its corresponding hardener (Epoxy Technology, USA).

Previously to the fabrication of different composites, the MWNTs were pre-treated with nitric acid (HNO_3) for improving their homogenization. Composites with different MWNT loading were tested through the evaluation of their electrical, morphological and electrochemical properties.

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