

PP149**MODIFICATION APPLICATION OF CARBON-PASTE ELECTRODE MODIFIED WITH FePc FOR VOLTAMMETRIC DETERMINATION OF EPINEPHRINE IN THE PRESENCE OF ASCORBIC ACID AND URIC ACID****SAEED SHAHROKHIAN*** and **MASOUMEH GHALKHANI***Department of Chemistry, Sharif University of Technology, Azadi Avenue, Tehran 11155-9516, Iran
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A carbon-paste electrode (CPE) bulk modified with iron (II)phthalocyanine is used for the sensitive voltammetric determination of epinephrine (EN). The electrochemical response characteristics of EN, ascorbic acid (AA) and uric acid (UA) at the surface of modified electrode is investigated by cyclic and differential pulse voltammetry (CV & DPV). The results show an efficient catalytic activity for the electro-oxidation of EN, which leads to improvement the reversibility and lowering the overpotential more than 100 mV. The effect of pH and potential sweep rate on the mechanism of the electrode process is investigated on the surface of modified electrode. This modified electrode exhibits a potent and persistent electron mediating behavior followed by well-separated oxidation peaks towards EN, AA and UA with good potential differences (AA-EN-UA: 128-345-485 mV). With respect to improved sharpness of the anodic waves on the surface of modified electrode, the resulted peak resolutions are large enough to determine EN in the presence of AA and UA. Under the optimum pH (4.0 by 0.1 M acetate buffer solution), the anodic peak current (in DPV measurements) versus the concentration of EN has a good linear relation in the range of 1 to 300 μM , with the correlation coefficient of 0.998 and the detection limit of 0.5 μM . The prepared modified electrode shows very good accuracy for voltammetric determination of EN in pharmaceutical and clinical preparations and excellent recovery results in spiking to these samples. High sensitivity and selectivity, sub-micromolar detection limit, very good reproducibility together with ease of preparation and regeneration of the electrode surface by simple polishing, make the electrode very suitable for the determination of EN in pharmaceutical and clinical preparations.

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PP150**INVESTIGATION OF THE ELECTROCHEMICAL BEHAVIOR OF CATECHOL AND 4-METHYL CATECHOL IN THE PRESENCE OF METHYL MERCAPTO THIADIAZOLE AS A NOCLEOPHILE: APPLICATION TO ELECTROCHEMICAL SYNTHESIS****SAEED SHAHROKHIAN*** and **SHOKOUFEH RASTGAR***Department of Chemistry, Sharif University of Technology, Azadi Avenue, Tehran 11155-9516, Iran
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One of the prime principles of green chemistry is to develop an alternative reaction medium, which is the basis for the development of many cleaner chemical technologies and electrochemical synthesis in water. Catechols are a promising group of compounds worthwhile for further investigation, which may lead to the discovery of selective acting, biodegradable agrochemicals having high human, animal and plant compatibility. Preparation and anticonvulsant activity of several derivatives of thiadiazoles have been reported previously. Potential anti-convulsant activities of 1,3,4-thiadiazole derivatives made it a good lead for the synthesis of new compounds. Electro-oxidation of catechol and 4-methyl catechol in the presence of 3-mercapto-5-methyl-1,3,4-thiadiazole as a nucleophile in aqueous buffered solutions was studied by cyclic voltammetry and controlled-potential coulometry. The mechanism of electrochemical reaction is confirmed by spectrophotometric tracing in various times of controlled-potential coulometry. The voltammetric and spectrophotometric foundations indicate that a 1,4 Michael addition of thiadiazole from its thiol moiety to the electrochemically derived *o*-quinone is occurred. The electrochemical synthesis of Michael addition product has been successfully accomplished by controlled-potential coulometry in a divided H-type cell and the reaction product was characterized by spectrophotometric, ¹H and ¹³C NMR, elemental analysis and mass spectrometric methods.

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PP151**MODIFICATION OF GLASSY CARBON ELECTRODE USING NAFION DOPED CARBON NANO PARTICLES: APPLICATION TO VOLTAMMETRIC DETECTION OF GUANINE IN THE PRESENCE OF ADENINE****SAEED SHAHROKHIAN^{a*}, ATEFEH TAHERI^a, and MANDANA AMIRI^b**^a Department of Chemistry, Sharif University of Technology, Tehran 11155-9516, Iran, ^b Department of Physics, Sharif University of Technology, Tehran 11365-9161, Iran shahrokhian@sharif.edu.ir

Detection of purine bases and purine-containing compounds represent a challenging and important task owing to the importance of these compounds in a variety of biochemical processes. Guanine and adenine are the building blocks of both DNA and RNA that play a crucial role in protein biosynthesis, and the storage of genetic information; in addition, guanine has the lowest oxidation potential and is believed to play a key role in the oxidation of DNA. Recently there have been considerable efforts in the development of electrochemical methods for detection of nucleic acids in biological samples based on guanine oxidation. In this work, a modified glassy carbon electrode using carbon nanoparticles (CNPs) doped with nafion was applied for voltammetric detection of guanine in the presence of adenine. Guanine and adenine produced well-defined oxidation peaks at about +0.6 and +0.9 V, respectively in pH 7 phosphate buffer. Application of the modified electrode resulted in a sensitivity enhancement of about three orders of magnitude in detection of guanine and a negative peak shift up to 0.08 V. The electrode was characterized by using electrochemical methods and atomic force microscopy (AFM). It was found that CNPs enhanced the electroactive surface area and accelerated the rate of electron transfer. Detection limit of guanine was found 1×10^{-7} M (S/N=3) by using differential pulse voltammetry and the linear range in these determinations was from 0.1 to 10 μ M. Acid-denatured DNA showed two oxidation peaks corresponding to guanine and adenine residues. The proposed method can be used to estimate the guanine contents in DNA with good selectivity and sensitivity.

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PP152**APPLICATION OF CONGO RED SUPPORTED ON MULTI-WALLED CARBON NANOTUBE FOR PREPARATION OF A MODIFIED ELECTRODE IN DETECTION OF URIC ACID IN THE PRESENCE OF GREAT AMOUNT OF ASCORBIC ACID****SAEED SHAHROKHIAN*, and HAMID REZA ZARE-MHRJARDI**

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Noncovalent immobilization of CR on multi-walled carbon nanotube (MWCNT) (via ultrasonic agitation in aqueous solutions) and its further incorporation within a nafion matrix is described. The prepared composite used for modification of carbon-paste electrode (CPE). The electrochemical response characteristics of uric acid (UA) and ascorbic acid (AA) at the surface of modified electrode is investigated by cyclic and differential pulse voltammetry (CV & DPV). The modified electrode in this work showed an effective and selective electrocatalytic activity for the anodic oxidation of UA and masking the effect of AA and sulfhydryl compounds, which usually considered as interferences in most of the reported modified electrodes. Incorporation of CNT in the matrix of the modified composite enhances the microscopic area and currents in voltammetric investigations. With the noncovalent functionalization by CR, CNTs are efficiently exfoliated into individual nanotubes. In addition, most of the irregular impurities on the sidewall of CNTs are removed, indicating the cleaning role of adsorbed CR. Another interesting feature of CR decorated CNTs is that one of the individual nanotube is bended to nearly a right angle at the middle part and tightly bound with another individual tube at the terminus via sidewall coupling, foreseeing the ability of water-soluble CNTs to form stable and complicated network nanostructures. The effect of pH and potential sweep rate on the mechanism of the electrode process is investigated on the surface of modified electrode. Under the optimum pH (7.0 by 0.1 M phosphate buffer solution), the anodic peak current (in DPV measurements) versus the concentration of UA has a good linear relation in the range of 0.6 to 100 μ M, with the correlation coefficient of 0.998 and the detection limit of 0.01 μ M. High sensitivity and selectivity and very low detection limit together with the very easy preparation and surface regeneration of the modified electrode and reproducibility of the voltammetric responses makes the prepared modified system very useful in the construction of simple devices for the determination of UA in the presence of large amount of AA in clinical and pharmaceutical preparations.

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PP153

A STRUCTURAL STUDY OF SURFACE SEGREGATION ON AgCu, AuBi AND AgBi MIXED ELECTRODES

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Increasing focus on environmental surveillance has led to an extensive search for new sensors suitable for electrochemical field analyses. Liquid mercury has in many areas been replaced by solid electrodes which represent an environmental friendly alternative, but solid electrodes in general have a low overpotential towards the hydrogen evolution reaction (HER) in water solutions, and lack the long time stability needed for continuous monitoring.

It has been observed that mixing a compound with low overvoltage towards the HER with only small amounts of a metal having high overvoltage towards HER increases the overall overvoltage towards HER for the mixed metal compound¹. However, an increase in overvoltage towards HER has also been observed for the alloys of silver and copper, two metals which have quite similar properties concerning the overvoltage towards HER². An additional improved property achieved with mixed electrode materials is increased long time stability¹.

The ionic structures (crystal structure) of various AgCu alloys and AuBi and AgBi mixed metal surfaces will be structurally characterized using surface extended X-ray absorption spectroscopy (SEXAFS). X-ray absorption spectroscopy (XAS) will be performed to probe long-range structural information of the mixed metals and alloys. From the absorption spectrum, information on structure around absorbing atom on the surface is achieved, and electronic transitions of the surface metals can be obtained from the pre-edge region of the absorption spectrum.

These results will in combination with results obtained from electrochemical characterization by cyclic voltammetry and electrochemical impedance spectroscopy give valuable information about the effect of surface segregation on HER and adsorption processes on alloys and mixed metal surfaces. Results from investigations of the adsorption of hydrogen on various surfaces performed with a scanning electrochemical microscope (SECM) will also be included.

By combining surface characterisation results obtained with the techniques mentioned, a complete picture of the chemistry of the different metals in the alloys is achieved. This information is very important for understanding how the structure of alloys and mixed electrodes influence the kinetics of the hydrogen evolution reaction.

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PP154

ELECTROCHEMICAL OXIDATION OF BERBERINE

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Berberine is an isoquinoline alkaloid occurring abundantly in plants *Hydrastis canadensis*, *Coptis chinensis* and *Berberis* gen. predominantly in the roots, rhizomes, bark and stems. It is used in traditional Chinese and Indian medicine especially to control blood glucose in diabetes¹, to treat gastroenteritis, diarrhea, to stimulate the immune system and displays anti-tumor, antimicrobial and many others biological and pharmacological activities². Protective effects of berberine against lipoprotein oxidation have been described recently^{2,3} showing the antioxidant properties of this compound.

Electrochemical behavior of berberine that can model its biological action has been studied only in reduction mode at a mercury electrode⁴. The goal of the presented work is to report our finding of electro-oxidation of berberine at a glassy carbon and a platinum electrode in nonaqueous and aqueous media in dependence of acidity. Cyclic voltammetry as well as liquid chromatography with amperometric detection were used for this study. The last-mentioned method was optimized for the determination of berberine in plant samples.

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PP155**STRUCTURES OF COBALT AND NICKEL
HEXACYANOFERRATE FILMS STUDIED BY EXAFS****MAGDALENA A. SKOPEK^{a,*}, STEVE J. GURMAN^b,
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Prussian Blue, the parent species of the numerous family of polynuclear transition hexacyanometallates, is one of the oldest synthetic coordination compounds known. This group of insoluble mixed-valence materials has attracted attention because of the potential application in sensors, batteries, electrochromic devices and optically switchable molecular compounds. There is considerable opportunity for manipulation of material properties by varying either the transition metals forming the network with the alternating cyanide bridges or the univalent alkali metal counter cations occupying interstitial sites. Hexacyanometallates have been studied as powders, pellets, guests in various types of matrices, single crystals or on modified electrodes, and their diversity of stoichiometry and structure are well known due to their high sensitivity to preparative procedures. External control parameters such as illumination, temperature or (as in the present study) applied potential can influence on a range of characteristics, such as electrochromic, thermochromic, ion-exchange, charge storage, mixed valence electrical conductivity, electrocatalytic, optical and magnetic behaviour.

Despite the fact that the quoted applications have generated a wealth of information on metal hexacyanides, structural ambiguities remain. Extended x-ray absorption fine structure (EXAFS) provides valence states, coordination numbers, interatomic distances, root mean square deviation of bond length (i.e. local order or Debye-Waller factor, $2\sigma^2$) and the elemental identities of neighbouring atoms. Since EXAFS can provide such information even for amorphous materials, or materials without long range structural order, it is ideally suited to characterization of electrodeposited thin films on electrode surfaces.

In our study we focus on two representative hexacyanometallates, nickel and cobalt hexacyanoferrate. They were potentiodynamically deposited as thin films on inert electrode surfaces. EXAFS measurements were made in fluorescence mode at Daresbury Laboratory, Warrington, UK, using beamlines 7.1 and 16.5. Measurements were taken at the Fe K-edge (at 7111 eV), the Ni K-edge (at 8333 eV) and the Co K-edge (at 7709 eV) as functions of applied potential. The EXAFS responses, when combined with x-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (IR), yield contrasting patterns of electroactivity and structural change for both materials.

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PP156**VOLTAMMETRIC STUDIES
OF 2-GUANIDINOBENZIMIDAZOLE****ŚLAWOMIRA SKRZYPEK^{a,*}, VALENTIN
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2-Guanidinobenzimidazole (2gb, Fig. 1) and some of its derivatives are biologically active compounds. They exhibit physiological activity, an example being the blocking of skin sodium channels. 2gb interacts through the guanidine group with the outward-facing channel entrance forming a labile complex. In addition, 2gb diminishes gastric acid secretion, and also exhibits hypoglycemic and hypotensive properties.

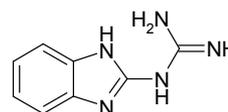


Fig. 1. 2-Guanidinobenzimidazole

In this study we demonstrate that 2gb catalyzes effectively the hydrogen evolution reaction at a static mercury electrode, which is the basis for its electrochemical characterization and determination. Electrochemical study was carried out by means of cyclic (CV), linear sweep (LSV), differential pulse (DPV), and square wave (SWV) voltammetry. It was observed that the voltammetric response depends on pH of the medium, composition and concentration of buffers, accumulation time and potential, as well as the critical time of the voltammetric experiment. Mechanistic aspects of the electrode reaction have been clarified by CV and SWV, recalling the previous theoretical model¹. The optimal conditions for analytical determination were obtained in a citrate buffer solution at pH 2.5. The electroanalytical procedure enabled determination of 2gb in the concentration range $6 \times 10^{-7} - 3 \times 10^{-6}$ mol L⁻¹ by LSV, $4 \times 10^{-7} - 2 \times 10^{-6}$ mol L⁻¹ by DPV, $1 \times 10^{-7} - 1 \times 10^{-6}$ mol L⁻¹ by SWV and $8 \times 10^{-8} - 9 \times 10^{-7}$ mol L⁻¹ by SW preceded by adsorptive accumulation. Repeatability, precision, accuracy of the developed methods just as detection and quantifications limits were determined.

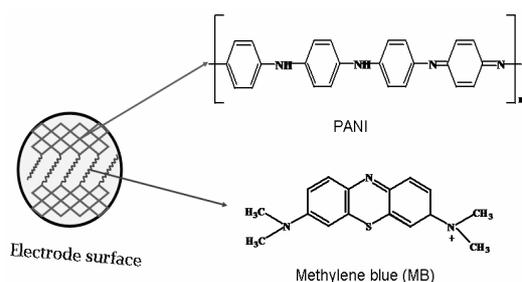
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PP157**DETERMINATION OF INORGANIC MERCURY USING A POLYANILINE AND POLYANILINE-METHYLENE BLUE COATED SCREEN-PRINTED CARBON ELECTRODE****VERNON SOMERSET^{a*}, JOY LEANER^a, ROBERT MASON^b, and EMMANUEL IWUOHA^c**

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Inorganic mercury ions (Hg^{2+}) in laboratory prepared solutions were determined with a screen-printed carbon electrode (SPCE) coated with either polyaniline¹ and polyaniline-methylene blue² polymer layers. The electrically-conducting polymers were prepared by chemical polymerisation of monomer solutions of aniline, and mixed solutions of aniline with methylene blue that were drop-coated onto a screen-printed carbon electrode afterwards. Anodic stripping voltammetry (ASV) was used to evaluate a solution composed of [1×10^{-6} M HgCl_2 , 0.1 M H_2SO_4 , 0.5 M HCl], in the presence of the two different polymer combinations. The Hg^{2+} ions were determined as follows, *i*) pre-concentration and reduction on the modified electrode surface, and *ii*) subsequent stripping from the electrode surface during the positive potential sweep. The experimental conditions optimised for Hg^{2+} determination included the supporting electrolyte concentration and the accumulation time^{3,4}. The detection limits for the [1×10^{-6} M HgCl_2 , 0.1 M H_2SO_4 , 0.5 M HCl] solution in the presence of the polyaniline and polyaniline-methylene blue modified SPCE were evaluated. The results of the study will be presented to report the use of a conducting polymer modified SPCE as an alternative transducer for the voltammetric stripping and analysis of Hg^{2+} ions.



Scheme 1. Screen-printed electrode surface coated with polyaniline-methylene blue for anodic stripping voltammetry of inorganic mercury ions

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PP158**ELECTROANALYTICAL STUDY OF PHOSPHOLIPID STRUCTURES****JITKA SOUČKOVÁ*, JANA SKOPALOVÁ, MAGDALENA MEGOVÁ, LUKÁŠ MÜLLER, and PETR BARTÁK**

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Our attention is devoted to study of behavior of phospholipid structures in aqueous solution. Phospholipids are amphiphilic molecules, analogous to other surfactants, forming in aqueous media different structures depending on their concentration. In higher concentration they form liposomes, polymolecular aggregates organized from closed phospholipid bilayer¹. These structures of varying size (generally 50 nm to 5 μm in diameter) can encapsulate hydrophobic compound in bilayer membrane or hydrophilic molecules in the internal cavity. Owing to these properties they are used in pharmacology, medical science, molecular biology, food and cosmetic industry for transport of biologically active compounds². Liposomes are more frequently employed in analytical chemistry as (pseudo)stationary phase in the separation techniques³. Recently phospholipid vesicles have been prepared by a new method, which is based on spontaneous revesiculation¹. We study this process of liposomes formation in aqueous phospholipid solution by the different independent electroanalytical methods: electrocapillary and conductivity measurements and linear sweep voltammetry. Last two methods were used for observation of the kinetics of spontaneous revesiculation.

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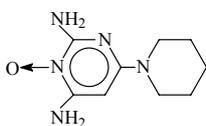
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PP159
GRAPHITE- POLYURETHANE COMPOSITE
ELECTRODES FOR STUDIES OF MINOXIDIL

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Minoxidil (MX) is a pharmaceutical compound that dilates blood vessels and is used in the treatment of arterial hypertension and in the treatment of *Alopecia Areata*¹.



The purpose of this work was to investigate the voltammetric behavior of MX using a graphite-polyurethane (PU) composite electrode (60 % graphite, w/w), without any surface modification. This new composite² has been previously shown to be sensitive and useful in cyclic and square wave voltammetric studies of hydroquinone and atenolol^{3,4}.

Cyclic voltammetry of MX was performed at the composite electrodes in solutions in the pH range 2.0 to 8.0. The best experimental conditions for electrooxidation of MX were found to be in pH 2.5 Clark and Lubs solutions (HCl/KCl) at scan rate 25 mV s⁻¹, the oxidation peak appearing at +0.860 V vs SCE. The linear range was from 6.0×10⁻⁶ to 3.0×10⁻⁴ mol L⁻¹, and the limit of detection was 1.5 μmol L⁻¹.

Square wave voltammetry showed a linear range from 2.0×10⁻⁶ to 1.0×10⁻³ mol L⁻¹, and limit of detection 8.0 μmol L⁻¹, using optimised experimental conditions of 50 mV amplitude, potential increment 5 mV, and frequency 25 Hz. Square wave voltammograms also demonstrated that the process is irreversible.

Electrochemical impedance spectra were recorded at different applied potentials in blank and in solutions spiked with MX; the results suggested that no adsorption of the MX or its oxidation products occurs on the electrode surface, which permits successive measurements without surface regeneration or renewal, confirming the voltammetric evidence.

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PP160
NAFION FILM COATED SILVER AMALGAM
ELECTRODE FOR DETERMINATION OF TRACE
METALS IN PRESENCE OF SURFACE ACTIVE
COMPOUNDS

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Anodic stripping voltammetry (ASV) is a highly sensitive and economically reasonable electroanalytical technique for measuring trace metals and one of a few techniques suitable for long time field monitoring of real samples¹.

Direct determination of trace metals in natural samples is often disturbed by presence of surfactants. These substances adsorb at the electrode surface and block it, disturbing deposition of the analyte². Such surface fouling is a limitation in practical ASV application in environmental samples and therefore a big challenge considering use of silver amalgam in long time monitoring stations in the field. The uncoated silver amalgam electrode slowly loses its sensitivity in samples with surface active compounds content during long time use.

This problem can be solved by applying a protective Nafion film layer to decrease adsorption of surface active compounds. Then surfactant species are mechanically blocked from reaching electrode surface, while small metal cations can diffuse through the Nafion membrane.

In this work, performance of silver amalgam electrode was investigated for zinc, cadmium and lead detection in aqueous solutions containing surface active compounds – humic acid and albumin. The performance of uncoated silver amalgam electrode and Nafion coated silver amalgam electrode was compared during repeated stripping experiments. Nafion coating increases sensitivity of the silver amalgam electrode and gives enhanced signal in samples with surface active compounds. The Nafion coating is easy to prepare and the protective effect has a significant value.

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PP161**LONG TIME MONITORING OF ZINC AND IRON IN WASTE WATER BY USE OF AN AUTOMATIC TRACE METAL SYSTEM****KRISTINA STRASUNSKIENE and ØYVIND MIKKELSEN****Dept. of Chemistry, Norwegian University of Science and Technology, N-7491 Trondheim, Norway
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Monitoring of natural water resources is now at extensive focus¹. Some recent developments and results in the field of remote monitoring of trace metals in waste water by use of automatic trace metal system (ATMS) are reviewed. This system can be set up to transmit data to computer networks, has a high measuring frequency with possibility for numerous measurements per day, low detection limit and is easy to operate². In this contribution the use of the ATMS for long time monitoring of trace metals is demonstrated. Zinc and iron have been monitored continuously every 30 minutes for a period of 7 months in waste by use of differential pulse anodic stripping voltammetry using solid silver amalgam electrode as a working electrode.

The system shows good calibration curves ($r^2_{\text{avg}} = 0.98$) and good stability. Manual maintenance like polishing of the working electrode and cleaning the cell system was carried out once every five days. Additionally, samples were collected manually and analyzed with ICP-MS to get the total concentrations of trace metals.

The possibility to frequently monitor trace metals is a great advantage comparing to random data received from manual sampling and analyses in laboratory. The successful use of solid silver amalgam electrode in waste water for long time monitoring demonstrates the wide range of application and opens new possibilities for environmental surveillance with minimal manual maintenance.

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PP162**DETERMINATION OF 5-NITROACENAPHTHENE BY ADSORPTIVE VOLTAMMETRY****C. VILASECA SUAÑA, LUCAS HERNÁNDEZ, JOSÉ VICENTE, and PEDRO HERNÁNDEZ****Dep. Química Analítica, Facultad de Ciencias, Universidad Autónoma de Madrid. 28049 Madrid, Spain
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In this work we are going to exposed the results obtained of the electrochemical analysis by square wave voltammetry of 5-nitroacenaphthene. This one is a compound belonging to the nitrogenous polycyclical aromatic hydrocarbons, which are derived from the polycyclical aromatic hy-

drocarbons in this case of the acenaphthene, with two or more aromatic molten rings. These compounds are given as direct or indirect products of the incomplete combustion by means of two different processes: Nitration during the processes of combustion, like in case of the gases of leak of the vehicles diesel, or his formation in the atmosphere from the aromatic polycyclical hydrocarbons.

The aim of this work is the study of 5-nitroacenaphthene due to his incorporation in the lists of carcinogenic substances.

For it an electrochemistry methodology will be design in order to identifier and qualifier the levels of 5-nitroacenaphthene presents in the water of rain. In the first moment the study of the electrochemical behaviour was carried out of 5-nitroacenaphthene by square wave voltammetry in electrode of drop of mercury. The results found on having optimized the physical and chemical variables are that the process is an irreversible reduction, giving a wave of reduction to a potential of -0.4 V. The optimal conditions of the method was used to quantifier and qualifier the presence of 5-nitroacenaphthene in the water of rain.

The authors thank the Spanish Education Ministry for financial support (Project CTQ2004-04142/BQU).

PP163**DETECTION OF DNA-HYBRIDIZATION WITH Au/Bi ALLOY ELECTRODES****ANNETTE-ENRICA SURKUS, HEIKO DUWENSEE, and GERD-UWE FLECHSIG****University of Rostock, Department of Analytical, Technical and Environmental Chemistry, Albert-Einstein-Str. 3a, D-18051 Rostock, Germany
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Beside the usual optical techniques of hybridization detection, electrochemical methods have also been applied increasingly during the last years. The main advantages are that they are inexpensive and easy to use as well as their high efficiency. Usually gold electrodes are used for the detection. There is a lot of scientific research working with other electrode materials, like bismuth^{1,2}. Bismuth as electrode material is increasingly used in heavy metal analysis³ because it is not toxic in contrast to conventionally used mercury, and it offers a high hydrogen overvoltage and adsorption affinity. Unfortunately the disadvantage of the bismuth is the relatively small corrosion resistance. The combination with gold as Au/Bi alloy should improve the corrosion resistance essentially⁴.

First investigations with Au/Bi alloy electrodes (96 % Au / 4 % Bi) demonstrated the assumption. After SAM-formation the hybridization with an [OsO₄(bipy)]-marked target was carried out. In addition the influence of the target-concentration and the time stability were examined using voltammetric methods.

In summary the results were compared with those at the pure gold electrode.

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PP164

**NANOSTRUCTURATED CONDUCTING POLYMER
BASED BIOSENSORS FOR THE ANALYSIS
OF PHENOLIC COMPOUNDS**

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Biosensors represent an interesting alternative for the detection of phenolic compounds. Many different approaches can be found in the literature including carbon-nanotube based biosensors^{1,2}, conducting polymer modified electrodes³, and silica sol-gel composite films⁴. Some of these methods are relatively complicated, require the use of several reagents and often the biosensor produced presents stability problems. For that reason new alternative biosensor designs for phenolic compounds are needed.

Biosensors based on nanostructured layers⁵ have demonstrated to be simple in preparation, allowing the easy electrostatic attractions of biomolecules with minimal protein denaturation during the adsorption process and offering a great promise for developing amperometric biosensors.

Screen-printed carbon electrodes, ITO-coated glass slides and Au electrodes have been modified in this work with polyaniline (PANI) conducting polymer nanolayers and used for the preparation of tyrosinase/laccase-based biosensors.

Optical and electrochemical characterisations have been performed during the preparation of the platforms and showed the efficiency of the Layer-by-Layer (LbL) technique used to modify the electrodes. Some preliminary results related to the detection of phenolic compounds achieved in batch and flow-injection systems and using the different platforms will be also shown.

This work has been done under the WARMER research project, FP6-034472. Authors thank also CAPES, CNPq and DQ-UFSCar for the given supports.

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PP165

**COPPER DETERMINATION IN ETHANOL FUEL
SAMPLES BY ANODIC STRIPPING VOLTAMMETRY
AT A GOLD MICROELECTRODE**

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A linear sweep anodic stripping voltammetric method was developed for copper determination in commercial ethanol fuel samples by using a gold microelectrode. Under the optimized conditions, it was obtained a linear range from 5.0×10^{-8} to 1.0×10^{-6} mol L⁻¹, with detection limit of 22 nmol L⁻¹. The developed method was employed to determine copper ions in six commercial ethanol fuel samples and the obtained results were compared with those obtained by FAAS. This study showed that for most of analyzed samples both methods produced concordant results. However, for two samples, copper is distributed in its labile and complexed forms leading to copper contents contrasting with those obtained by flame atomic absorption spectroscopy (FAAS). It was observed that acidification of the samples is a very efficient way to recover copper from its complexed forms. After acidification, the copper contents obtained were concordant with those obtained by FAAS for all analyzed samples. The results obtained in this work have demonstrated that a gold microelectrode can be successfully employed for copper determination directly in commercial ethanol fuel samples. The proposed method provides some great advances in electroanalysis of copper in this kind of matrix once this is the first work in which both preconcentration and detection step is performed directly in commercial samples without supporting electrolyte addition or pretreatment steps. Thus, the developed method allows copper determination in a fast and simple way with low reagent consumption. Moreover, this work is the first in literature using an electroanalytical technique to provide some insights about the speciation of copper in commercial ethanol fuel samples. The obtained results have shown that acidification of the samples is a very efficient way to recover copper from its complexed forms. In addition, this procedure does not introduce systematic errors in the proposed method.

PP166**ANTIMONY- vs. BISMUTH-MODIFIED CARBON PASTE ELECTRODES AND RELATED SENSORS IN ELECTROCHEMICAL STRIPPING ANALYSIS****EVA TESAROVA^{a*}, LUCIE BALDRIANOVA^a, SAMO B. HOCEVAR^b, IVAN SVANCARA^a, RADOVAN METELKA^a, BOZIDAR OGOREVC^b, and KAREL VYTRAS^a**

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Antimony and bismuth as the elements of the same group in the periodical system possess similar properties as well as practical usage and e.g. their related behavior in potentiometric pH-measurements is known for more than 80 years¹.

While bismuth-based electrodes are now intensively used in voltammetric measurements as one of the most promising alternative to mercury electrodes², related antimony electrodes were of marginal interest until very recently. In contrast to some initial experiments concerning carbon paste electrodes or carbon screen-printed electrodes modified with solid antimony(III) oxide^{3,4}, newly examined antimony electrodes (namely: antimony film-plated glassy carbon electrode, SbF-GCE⁵ and carbon-paste based analogue, SbF-CPE⁶), have been shown to be fairly applicable in more acidic supporting media. In this contribution, some advanced investigations on SbF-CPE, together with initial characterisations of two newest variants, antimony powder-modified carbon paste or carbon ink (Sb-CPE and Sb-SPE, resp.), are discussed in association with possibilities and limitations in electrochemical stripping analysis of heavy metals at the trace concentration level.

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PP167**ROLE OF HYDROGEN EVOLUTION ON THE REDOX PROCESS OF GUANINE****LIBUŠE TRNKOVÁ***

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More than 25 years it has been known that the nucleobase guanine (G) is reduced on a mercury electrode at negative potentials and its reduction signal is not detectable due to overlapping with the process of hydrogen evolution or the discharge of components of supporting electrolytes^{1,2}. Using macroscale controlled potential electrolysis in combination with NMR, the reduction product as 7,8-dihydroguanine was confirmed³. The microscale electrolysis at mercury electrode recorded by fast scan rates showed that the reduction product can be oxidized back to the original molecule G exhibiting an anodic signal at around -0.2 V vs. Ag/AgCl/KCl. The anodic G peak is very analytically useful because the N7 position of G represents the preferred binding sites of antitumour agents, metals or mutagenic substances. The G peak is regarded as an indicator of (a) structure of oligo- and polynucleotide changes, (b) interaction with components in solutions, and (c) different types of covalent adducts⁴. The contribution is aimed at explaining the role of hydrogen reduction (HER) in the redox process of guanine. To elucidate the interrelationship of HER and reduction of guanosine we studied these processes in aqueous solution with tetraethylammonium perchlorate by cyclic voltammetry and elimination voltammetry with linear scan (EVLS)⁵ with forward and backward scans. Therefore the negative switching or starting potentials were changed and both reduction processes were evaluated.

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PP168
THE EFFECT OF THICKNESS OF A CAPILLARY WALL ON THE RESPONSE OF CONTACTLESS CONDUCTIVITY DETECTOR

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Capacitively coupled contactless conductivity detectors (C⁴D) of axial construction have been introduced for applications in capillary electrophoresis in 1998 (ref.^{1,2}). The construction comprises two tubular electrodes that are placed around the surface of the silica capillary. Conductivity is measured as the ac-current flowing through the solution phase inside the capillary in response to the high-frequency voltage applied to the two electrodes, which allows suppressing the capacitance component of the total impedance³. The distance between the surface of tubular electrode and the inner capillary surface is for the standard fused-silica capillaries typically around 150 μm.

In the present study the effect of thickness of a capillary wall on the response of C⁴D is investigated by performing the conductivity measurements in the non-standard capillaries with a much lower wall thickness of ca. 40 μm, which presumably should further suppress the capacitance component. The effect is demonstrated for two background electrolytes, namely, morpholinoethanesulfonic acid (MES)/histidine (His), and the aqueous solution of acetic acid in the broad concentration range.

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PP169
AMPEROMETRIC BIOSENSOR BASED ON ACETYLCHOLINESTERASE FOR PARAOXON DETECTION

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As consequence of increasing use of chemicals and biologically active compounds in chemical industry and agriculture, the environmental analytical community continues to

search for portable analytical techniques that can give reliable, *on-site* results for a variety of matrices and analytes, as for example pesticides. The toxicity of organophosphorous pesticides is attributed to their ability to inhibit acetylcholinesterase (AChE), which catalyses the hydrolysis of the neurotransmitting agent acetylcholine (ACh). Particularly, the AChE-based biosensors could be used as alarm systems, able to provide an estimation of the global toxicity index of food products or environmental samples¹.

A simple, reproducible and stable AChE amperometric bioelectrode²⁻³ was used following two experimental protocols, for measuring the enzyme activity before and after the incubation with paraoxon aqueous solution or dissolved in polar and non-polar solvent. The inhibitory effect of the pesticide induces a decrease of the catalytic activity of AChE. Consequently, less thiocholine (TCh) was produced from ATCh and the current value, due to the TCh oxidation was lower than that recorded in the blank solution and this difference could be correlated with the pesticide concentration.

The aim of this paper was to evaluate the type of inhibition induced by the aqueous paraoxon solution. Also, to demonstrate the influence of polar (acetonitrile) and non-polar (*n*-hexan, *n*-heptan) organic solvents on the activity of the immobilized AChE on a bioelectrode, as well as the synergetic influence of these solvents on the inhibition process induced by paraoxon. A kinetic analysis of the AChE-pesticide interaction process, using Hanes-Woolf linearisation and secondary plots for evaluation of equilibrium dissociation constants, allowed identifying the type of inhibition process. In the same time, the amperometric bioelectrode response allowed evidencing the influence of the organic solvents on the mechanism of AChE inhibition by paraoxon.

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PP170
SURFACE GRADIENTS ON BIPOLAR ELECTRODES

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In this contribution, we describe the use of electric fields and imaging optics to produce and analyze surfaces having gradients in chemical properties or molecular functionality. Such surfaces are highly attractive in e.g. sensor and biomi-

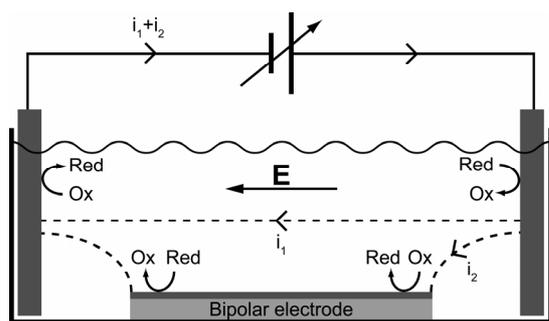


Fig. 1. Schematic experimental setup, showing the current paths when electrochemical reactions take place on the bipolar electrode. A variable voltage source is used to control the total current between e.g. two stainless steel electrodes

metic applications. To create a surface gradient, we use a bipolar electrode as a means of establishing a potential gradient across a surface¹. A voltage (or current) source and two electrodes are used to electrochemically induce an electric field in a solution in which a conducting surface is placed (see Fig. 1). The latter surface can then become a bipolar electrode, i.e. an electrode acting both as an anode and cathode. This occurs when the electric field parallel to the surface exceeds a certain threshold value and thereby induces redox reactions at both ends of the surface. A potential gradient across the electrode is thus induced by the electric field in the solution rather than by controlling the potential of the electrode. Since the potential difference between a point on the bipolar electrode and the solution will vary laterally along the surface, the rates of the reactions will also vary laterally. If the result of such reactions on either end of the bipolar electrode is the adsorption or desorption of a specific molecule, a gradient of that molecule can be created on the surface.

We have used imaging surface plasmon resonance (iSPR) to visualize the electrochemical reactions² on a bipolar electrode in real-time. If the refractive index of the solution close to the surface changes when species are being oxidized or reduced, the SPR response will change accordingly. In this way, the potential distribution over the bipolar electrode can also be visualized. We have also used imaging ellipsometry, which via thickness measurements provides a convenient way to evaluate the different steps in the formation of molecular gradients.

Different gradients for various applications can be formed using this method. We have for example prepared gradients of copper as well as of electropolymerized polypyr-

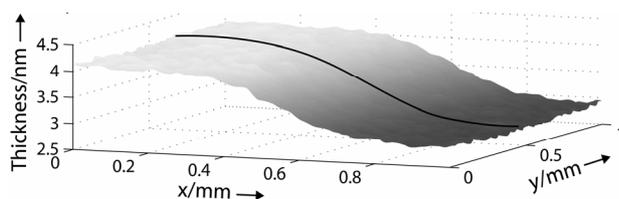


Fig. 2. Thickness map of the protein gradient with a line in the region from where the line profile was taken

role on gold. As a demonstration of the possibility to straightforwardly design and modify surfaces containing chemical property gradients, and the attachment of biorelevant molecules to such surfaces, we have used self-assembled monolayers (SAMs) and protein immobilization procedures. A two-component gradient of thiols was created and lysozyme was coupled to one of the thiols, resulting in a protein gradient. Using imaging ellipsometry, a thickness map of the gradient region was obtained (Fig. 2).

The present method is a fast and straightforward and does not require access to advanced laboratory equipment. The non-contacted surface can be of virtually any thickness, shape and material. A wide variety of different setup geometries and electrolytes can also be used, making it a very versatile approach. Future studies will include investigations of the composition, degree of phase separation, and organization of thiol gradients using ESCA, scanning probe techniques and FT-IR microscopy. Different gradient geometries will also be investigated, and details and results from these experiments will be presented.

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PP171

POROUS MICROELECTRODE ARRAYS FOR NEUROSCIENCE APPLICATIONS

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In order to understand the dynamics of large neural networks, one of the challenges of nowadays neuroscience is to reach the possibility to record large ensembles of neurons simultaneously. In this context, multielectrode arrays (MEA) are gaining a rapidly growing interest. These techniques consist in positioning arrays of microelectrodes in contact with the neural tissue in order to record in parallel a large number of cells. Beside these recording possibilities, MEA also offer the possibility to deliver electrical microstimulations to the neural networks. Another key challenge finally also consists in functionalizing microelectrodes in order to directly detect chemical activity (neurotransmitter release, e.g., glutamate) at the cellular level. However, three major problems become limiting factors when the size of the microelectrodes becomes small :

- 1) the intrinsic noise level (thermal noise) of the electrode

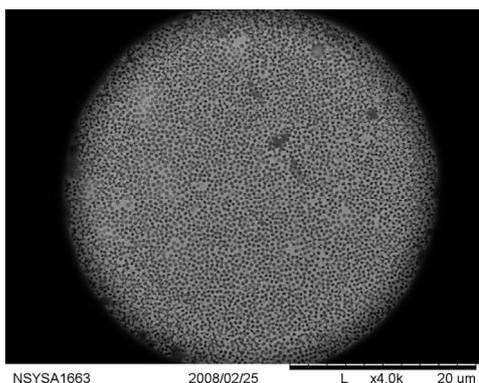


Fig. 1. SEM image (top view) of one porous planar microelectrode (30 microns diameter) out of a MEA containing 60 electrodes of this type, used for neurobiological applications

- 2) the current that can be injected without damaging the electrode material and the neural tissue becomes small and often not sufficient to stimulate the surrounding neurons, and
- 3) the sensitivity of chemical detection remains poor with a typical microelectrode ($\sim 100 \mu\text{m}^2$) and much larger electrodes are still required thus preventing detection at the cellular level.

We try to overcome these three limitations by using porous electrodes^{1,2}, and especially porous microelectrodes recently proposed as analytical tools^{3,4}. In order to combine the advantages of an overall small geometric surface with an active surface that is increased by one or two orders of magnitude, standard MEAs are covered with a highly porous metal overlayer. This is achieved by adapting the standard template technique⁵ and leads to well defined surfaces as illustrated in Figure 1. These engineered surfaces provide a lower intrinsic noise level for neural network recordings, and increased charge injection efficiency for electrical microstimulation of the central nervous system⁶.

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PP172

AMPEROMETRIC DETECTION OF NADH WITH CARBON PASTE ELECTRODE INCORPORATING CALCIUM-EXCHANGED ZEOLITE AND METHYLENE BLUE

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Nicotinamide adenine dinucleotide (NADH) is one of the most important coenzymes in the human brain and body. This coenzyme is a common cofactor of about 500 dehydrogenases and its reversible regeneration is a key step in the development of amperometric sensors¹. The zeolites offer the most complete range of interesting properties required at an electrochemical interface, including shape, size and charge selectivities, physical and chemical stabilities, high ion exchange capacity in a microstructured environment and hydrophilic character. The channels and the cavities of a zeolite framework offer ideal space for incorporation, stabilization and organization of these complex compounds, which often can play the role of redox mediators in different electrode processes². The catalytic nature, activity and other properties of zeolites can be greatly improved by cation-exchange. The versatile cation-exchange behavior of zeolites allows a large number of metal ions and complexes to be incorporated into these materials³.

In this context, new composite electrode materials consisting of Methylene Blue (as redox mediator), a synthetic zeolite (mesoporous zeolite 13X, Aldrich and a calcium-exchanged zeolite) (as immobilization support) and carbon paste matrix (as conductive material) were designed and tested for NADH amperometric detection. Methylene Blue is a water-soluble cationic dye molecule, suitable to catalyze NADH oxidation⁴⁻⁶.

The electrochemical properties (formal standard potential, peak currents and peak-to-peak separation) were different in the case of the calcium-exchanged zeolite, probably owing to the formation of a complex between mediator and Ca^{2+} . Cyclic voltammetry, rotating disk electrode and amperometry were used to study NADH electrocatalytic oxidation at low overpotentials (0 mV vs. $\text{Ag}/\text{AgCl}/\text{KCl}_{\text{sat}}$).

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PP173**AMPEROMETRIC IMMUNOSENSORS FOR OCHRATOXIN A WITH GOLD NANOPARTICLES ON SCREEN PRINTED ELECTRODES IN STATIC AND FLOW MICROSYSTEMS****JUAN C. VIDAL***, LAURA BONEL, PATRICIA DUATO, and JUAN R. CASTILLO

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Ochratoxin A (OTA) is a mycotoxin produced by several *Aspergillus* and *Penicilium* fungi species growing in different agricultural commodities in the field or during feed and food storage. OTA has nephrotoxic, teratogenic, carcinogenic and immunotoxic activity in human and animals. OTA occurs in several foodstuffs such as cereals, coffee beans, nuts and cocoa. There are very strict mycotoxin regulations all over the world¹. As an instance, the Standing Committee for Foodstuffs recently proposed E.U. regulatory limits for OTA in some agricultural commodities at very low ppb levels.

Official analytical methods available for the analysis of mycotoxins in food and foodstuffs are usually validated on AOAC International Official Methods of Analysis. For OTA, official HPLC methods are available for barley, corn, wheat, coffee, beer, milk, nuts, and wine².

Immunochemical methods exhibit high sensitivity and acceptable performance. Many immunological ELISA (enzyme-linked immunosorbent assays) methods are also widely used for *in-situ* and also in screening analysis³.

The direct voltammetric analysis of OTA is possible⁴, because of their electroactivity, but the oxidation of this molecule needs a very high potential (+1.5 V). Besides, sensitivity is low, and then the direct amperometric determination of OTA is not suitable at the level of low-ppb required. For these reasons, using amperometry the use of immobilized antibodies is more convenient.

The aim of the present work is to develop rapid and sensible OTA immunosensors using advantages of the immunochemical assay and the screen-printed technology.

We used indirect immunoassays in a competitive way by immobilizing OTA-BSA conjugate on the screen-printed carbon electrodes (SPCEs) and using AP (or HRP) labelled anti-OTA antibodies. Also we used labelled secondary anti-IgG antibodies to generate the amperometric signal, and poly(vinyl)alcohol or bovine serum albumin (BSA) for blocking and avoid unspecific adsorption.

The electrochemical substrate for generating the amperometric signal was 1-naphthyl phosphate (1-NPP). The enzymatic product, 1-naphthol, was detected by differential pulse voltammetry (DPV). The regeneration of the SPCEs was also assayed.

We also studied the influence of gold nanoparticles (AuNPs, 20 nm diameter) on the amperometric signals of the enzymatically generated 1-naphthol. They were electrochemically deposited from AuCl₄⁻ or directly immobilized from stabilized colloidal gold on the working electrode of the SPCEs.

Previously to design the amperometric immunosensors, ELISA checkerboards were assayed for characterizing the OTA-BSA and anti-OTA binding capacities and for optimizing the antibody and antigen dilutions. In these procedures, we used the same OTA-BSA conjugate and labelling with alkaline phosphatase the anti-OTA and anti-IgG, then using 4-nitronaphthyl phosphate as substrate. The enzymatic product 1-nitronaphthol was spectrophotometrically determined at 405 nm.

The use of AuNPs on SPCEs improved the electrochemical determination of the 1-naphthol. An increased amount of immobilized OTA-BSA conjugate was also observed, and the nanoparticles did not influence the immunoreactions of the OTA with the antibodies

The results obtained with the amperometric immunosensors were compared with official AOAC methods based on HPLC with fluorescence detection (*tr*: 5.57 min, flow speed: 1.2 ml min⁻¹, mobile phase: acetonitrile/water/acetic acid; $\lambda_{\text{exc}}=332$ nm, $\lambda_{\text{em}}=457$ nm)³.

This work include the use of a synthesized OTA-*mimic* molecule to be determined with SPCEs immunosensors and their analytical and immunological (ELISA) properties. It is a similar molecule to OTA (we present this molecule to ESEAC-08 in another presentation based on a quartz-crystal microbalance immunosensor), but it is less toxic and more economic than natural OTA.

In conclusion, SPCEs immunosensors for OTA allow the quick and specific determination of this mycotoxin at the ppb levels. The formation of a layer of nanostructured particles (AuNPs) increased the sensitivity of the developed OTA immunosensors.

This work has been financed by the Aragon Government (Science, Technology and University Department) with Project PM 027/2007. Patricia Duato thanks ACP S.A. a research grant.

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PP174**ELECTROCHEMICAL QUARTZ-CRYSTAL MICROBALANCE IMMUNOSENSORS FOR NATURAL AND SYNTHETIC OCHRATOXIN A****JUAN C. VIDAL***, PATRICIA DUATO, LAURA BONEL, and JUAN R. CASTILLO

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Identification and determination of mycotoxins in foods at the nanogram level is nowadays of extremely importance owing to their wide presence and the adverse effects in human

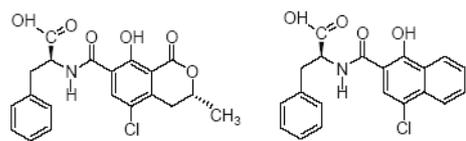


Fig. 1. a) OTA, b) OTA-mimic

(and animal) health. There are a great interest in Europe and many other countries in early detection and prevention strategies for decreasing mycotoxin contamination in foods. Legislation in the European Community strictly regulate the maximum contents of mycotoxins (concentration levels from about 0.01 to 10 ppb depending of the kind of food) in foods like cereals, wine, milk, nuts or dried fruit. From all of the wide range of mycotoxins (aflatoxins, deoxyvalenol, zearaleonone, fumonisins...), ochratoxins stands out because of their great toxicity and carcinogenicity.

We show the design, optimization and construction of immunosensors^{1,2} for Ochratoxin A (OTA), the more toxic ochratoxin, based on an electrochemical quartz-crystal microbalance transducer (*QCM*). The advantage of this technique is the absence of need for labeling (the antigen or antibody) as it is usual in immunoassays, ELISAs (enzyme-linked immunosorbent analysis) and other kind of immunosensors (e.g. fluorescent or amperometric).

The *QCM* offers the possibility of measuring very small mass changes ($\sim 18.5 \text{ ng/Hz cm}^2$) due to reaction of immobilized OTA conjugate (OTA-BSA) with Anti-OTA in a competitive way. An indirect immunoassay was preferable due to the small molecular weight of the analyte.

The use of biosensors for the *in situ* analytical determination of OTA is evident, but due to the very low levels of OTA in legislative demands, more sensitivity was preferred. Then, we used gold nanoparticles on the Au-quartz surface in order to improve sensitivity of the analytical response.

Gold surface of the quartz crystal was functionalized with a nanostructured self assembled monolayer (SAM), and then gold nanoparticles and the OTA-BSA conjugated were immobilized on the modified metal surface. It was demonstrated that gold nanoparticles (AuNPs, diameter 20 nm) increases the real sensor surface, and then more antigen conjugate (OTA-BSA) molecules were immobilized. Also a greater immunological binding capacity of the OTA-BSA to anti-OTA antibodies was observed with AuNPs.

We developed a static system arrangement in order to avoid viscosity and density effects (viscoelasticity of the fluids) caused by flowing liquids. We used urea 8 M. for immunosensor regeneration.

On the other hand, a less toxic OTA-mimic (see Fig. 1) molecule was chemically synthesized³ and analytically used onto this *QCM*-immunosensor. We compare analysis of the natural OTA with the *QCM* transducer nanostructured immunosensor with a validated high-performance liquid chromatography with a molecular fluorescence detector method (*HPLC-FD*).

Moreover, the gold surface roughness⁴ was determined in order to know the real area of the electrode for a reproduc-

ble formation of high quality immunosensors. Cyclic voltammetry was used for this purpose. Also we calculated the Sauerbrey's calibration constant of our system (C_f)⁵ with three electrochemical methods (Cyclic and differential-pulse voltammetry and chronoamperometry).

Besides, molecularly imprinted polymers (*MIPs*) were made using OTA-mimic^{3,6}, methacrylic acid as functional monomer, 2,2'-azobisisobutyronitrile (*AIBN*) as initiator and ethylene glycol dimethylacrylate (*EGDMA*) as cross linker. These *MIPs* are being used as stationary phase in SPE columns in a flow system connected to a HPLC pump and a fluorescence detector to study elution process and quantification of the OTA. Also, immobilized *MIPs* on gold surface of the *QCM* crystal are being tested as immunosensors⁷. In this case, the functional monomer of the *MIP* was 4-vinylpyridine, initiator was benzophenone and cross linker was divinylbenzene.

This work has been financed by the Aragon Government (Science, Technology and University Department) with Project PM 027/2007. Patricia Duato thanks ACP S.A. a research grant.

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PP175

BIOSENSORIC MEASUREMENTS OF L-ASCORBIC ACID AND POLYPHENOLS IN WINE AS FOOD MATRIX

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The characterization of different food samples and food ingredients carries great importance in food quality management as well as in developments of production processes. Because of their structure polyphenols¹ and antioxidants like ascorbic acid² are biologically active compounds occurring in many different foods. L-ascorbic acid is widely used as colour stabilizer and natural preservative, since it can highly protect food attributes by preventing oxidation that occurs during

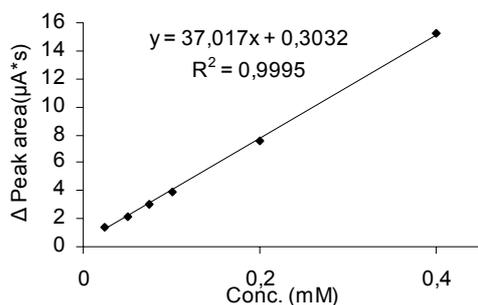


Fig. 1. Calibration curve of L-ascorbic acid; (400 mV, 100 mM acetate buffer pH 4.7)

processing and storage. Besides polyphenols have an influence on colour, flavour and taste, and they can increase wine quality and hygiene due to their anti-bacterial properties³. Different enzyme based biosensors could be used for measurement of these analytes, since they are ideal for quick analysis combined with their resistance for most of interfering components present in general food matrices⁴.

In our work enzyme based amperometric biosensors used in flow injection analyzer system were investigated. For detection of analytes ascorbate oxidase and laccase enzyme was immobilized on a natural protein membrane with glutaredialdehyde and fixed into a thin-layer enzyme cell separately from the amperometric detector^{5,6}. During the enzymatic reactions the amount of L-ascorbic acid and well defined polyphenols is decreasing, which could be detected at 400mV and 100mV polarizing potential. Using the difference value of enzymatic signal and background signal measured by two sample injectors, one before and one after the enzyme cell, the matrix effect of the real food samples (like in wines) is eliminated.

After optimization of measuring parameters for both systems (flow rate, ionic strength and pH of buffer solution, the working potential, temperature) calibration was carried out with ascorbic acid and catechin standard solutions (fig. 1

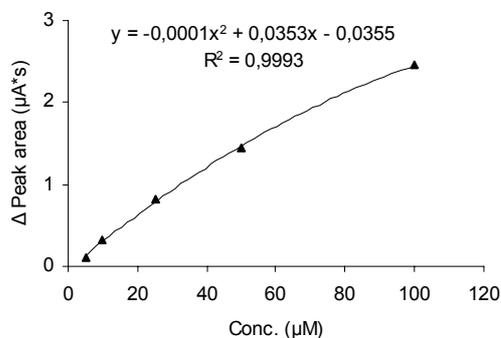


Fig. 2. Calibration curve of catechin; (100 mV, 200 mM acetate buffer, pH 5.5)

and fig. 2). After the statistical evaluation of the measuring system, the spiked ascorbic acid and polyphenol content of wine samples were measured to demonstrate the usability of developed biosensor. The results for content of polyphenols was verified and compared with HPLC method.

Special thanks to all colleagues and EgerFood Regional Research Center application 9/2005 for ensuring research background.

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PP176

CARBON NANOTUBE FIBER MICROELECTRODES AS SELECTIVE ANALYTICAL TOOLS

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Carbon nanotubes (CNT) have attracted considerable attention in recent years because of their remarkable electronic and mechanical properties^{1,2}. Their unique features make them extremely attractive for a wide range of sensing applications especially due to their ability to promote electron – transfer reactions^{3–5}. Here, we report on the preparation and interesting electrochemical behaviour of CNT fiber⁶ microelectrodes (MFCNT). By combining the advantages of CNTs with those of fiber electrodes, this type of microelectrode⁷ differs from CNT modified or CNT containing composite electrodes⁸, because it's made exclusively of CNT without any other component like additive or binder. These electrodes have been characterized, among others, with respect to the electrocatalytic oxidation of analytes via deshydrogenase mediated reactions. In this context they have been modified with mediator and their performance could be optimized by increasing the alignment of the nanotubes in the fiber and by increasing the active surface area through a partial exfoliation⁹, leading finally to interesting analytical tools¹⁰. The unmodified CNT fiber electrodes show also a very interesting intrinsic selectivity towards certain analytes of biological or

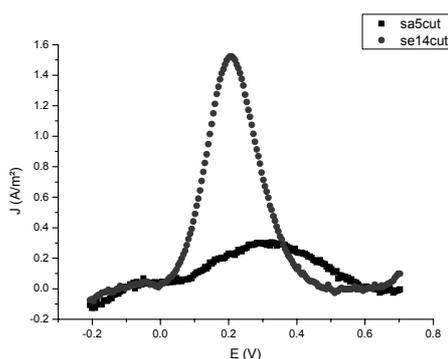


Fig. 1. Comparison of the reactivity of the CNT fiber electrode with respect to ascorbic acid: stretched fiber with aligned CNTs (red dotted line), unstretched fiber with less organized CNTs (black line)

medical importance. We could for example demonstrate¹¹ that these new tools are able to discriminate very efficiently ascorbic acid and dopamine, simultaneously present in an electrolyte solution, and this selectivity can be controlled by the alignment of the nanotubes in the fiber electrode (see Fig. 1).

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PP177

DETERMINATION OF SELENIUM IN RICE SAMPLES BY USING SQUARE WAVE VOLTAMMETRY

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Most of the dietary selenium comes from grain foods such as rice that is a principal food in Thailand. The square wave voltammetric determination of selenium (IV) at a glassy carbon electrode in the presence mercury ions is described. This method was performed in acetate buffer, pH about 4.7 and 0.3 M EDTA. Analytical characteristics of the method proved to be very satisfactory and it is currently being used for foodstuff studies. The concentration of selenium (IV) in acid digestions of rice samples has been determined by using standard addition method and the results were compared with those obtained by a spectroscopic technique. This method can be successfully applied for the determination of selenium in different Thai rice samples.

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PP178

VOLTAMMETRIC DETERMINATION OF GENOTOXIC 9-FLUORENONE AT MENISCUS MODIFIED SILVER SOLID AMALGAM ELECTRODE

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The influence of various genotoxic substances on environment and human health is of great importance. The sensitive and selective methods are necessary for the determination of these compounds in complicated matrices. Modern voltammetric techniques can in certain cases fulfill these demands. The studied compound 9-fluorenone (9-FN), known as proven genotoxic agent and structural unit of its carcinogenic nitro derivatives¹, has been determined at meniscus modified silver solid amalgam electrode² (m-AgSAE) – a non-toxic alternative to traditional mercury electrodes.

The stock solution was prepared in methanol due to the lower solubility of 9-FN in water. Optimal conditions for 9-FN determination have been investigated in buffered aqueous-methanolic solution. DC voltammetry (DCV) and differential pulse voltammetry (DPV) at m-AgSAE were used. The influence of pH at voltammetric behavior of 9-FN was investigated.

tigated in methanol – Britton-Robinson buffer solutions (1:1). The concentration dependences were measured under optimum conditions. Limit of determination was around 10^{-6} mol L⁻¹ for DCV at m-AgSAE and 10^{-7} mol L⁻¹ for DPV at m-AgSAE. Obtained results have been compared with previous determination of 9-FN at mercury electrodes³. An attempt to increase sensitivity using adsorptive stripping voltammetry at m-AgSAE was made. Cyclic voltammetry at m-AgSAE was used to investigate mechanism of reduction of 9-NF at m-AgSAE.

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PP179

DISSYMETRIC CARBON NANOTUBES BY BIPOLAR ELECTROCHEMISTRY

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We have recently reported an extremely simple « top-down » approach for the generation of carbon nanostructures. After the treatment of a sample of carbon black or HOPG with a polyoxometalate solution stable suspensions of carbon nanoparticles¹ and graphene sheets² are obtained respectively. A similar approach can also be used to solubilize carbon nanotubes³. These stable suspensions can then be used as a starting point to modify the carbon nanostructures with a metal layer.

Two alternative routes have been used for the metal deposition on these nanoobjects :

- a) a simple chemical process based on the metal generation by dismutation⁴. In this case the carbon nanostructures act as nucleation points and a homogeneous metal film is formed.
- b) an original process based on bipolar electrochemistry⁵, allowing the electrodeposition of metal on the nanostructure

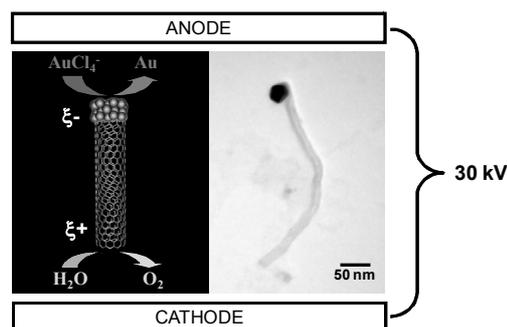


Fig. 1. Reaction scheme for the site selective generation of a metal cluster (left); TEM image of a MWCNT, modified at one end with a gold cluster using the bipolar electrodeposition approach (right)

without direct contact to an electrode. For that, the stabilized suspension of nanotubes is introduced in a capillary containing an aqueous metal salt solution and a high electric field is applied to orientate and polarize the individual tubes. During their transport through the capillary under sufficient polarization (30 kV) each nanotube is the site of water oxidation on one end, and the site of metal ion reduction on the other end. The size of the formed metal cluster can be controlled and is proportional to the potential drop along the nanotube⁶. This second procedure leads naturally to a highly controlled dissymmetric metal deposition as can be seen from the example of selective gold deposition on one end of a nanotube illustrated in Figure 1.

This method can be generalized to generate other Janus type nanoobjects and also to form deposits of a very different nature such as other metals, semiconductors or polymers. The approach therefore opens up the way to a whole new family of experiments leading to complex nanoobjects with an increasingly sophisticated design.

The two presented methods are complementary and can be used to tailor nanoobjects with a large variety in shape and morphology, interesting for several applications in the field of nanoscience in general and in particular in analytical chemistry.

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PP180**TRACE DETERMINATION OF DNA IN AN AMARYLLIDACEAE PLANT, *Narcissus tazetta* BY SQUARE-WAVE STRIPPING VOLTAMMETRY BASED ON GUANINE SIGNAL****YAVUZ YARDIM^a, ZUHRE SENTURK^{a*}, MEHMET OZSOZ^b, KEREM OZDEMIR^c, and EKREM ATALAN^c**^a Department of Analytical Chemistry, Faculty of Science and Letters, Yuzuncu Yil University, Van 65080, Turkey,^b Department of Analytical Chemistry, Faculty of Pharmacy, Ege University, Izmir 35100, Turkey, ^c Department of General Biology, Faculty of Science and Letters, Yuzuncu Yil University, Van 65080, Turkey
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The bioactive compounds of Amaryllidaceae species, which is one of the largest family of ornamental bulbous plants, are known to possess a wide variety of biological activities including antitumor, antiviral, cytotoxic, anti-inflammatory, antinociceptive, anticholinergic and DNA-binding activities. In view of the potential biopharmacological importance of this family, it is worthwhile to determine the amount of DNA in its species for future studies and potential biotechnological applications perhaps in medicine. The largest genus of Amaryllidaceae, *Narcissus* is naturally grown as well as cultivated in some part of Turkey.

To the best of our knowledge, no literature has been recorded for the determination of DNA in plants by using electrochemical DNA biosensor. In this study, the application of disposable electrochemical DNA biosensor to plant samples is presented.

The DNA biosensor was assembled by immobilizing the double-stranded fish sperm DNA on the surface of a pencil graphite electrode. Square-wave voltammetric scan with the baseline correction was carried out to evaluate the oxidation signal of guanine base. The experimental variables (solution pH, the buffer concentration, immobilization time, stirring speed, square-wave parameters) were carefully investigated. Under the optimal conditions, the increase of the peak was proportional to the DNA concentration in the linear range of 10–50 ng mL⁻¹. The extremely low detection limit (0.36 ng mL⁻¹) was coupled to a good surface-to-surface reproducibility (a relative standard deviation of 7.59 % for five repetitive measurements of 40 ng mL⁻¹). The renewable and low-cost DNA biosensor was successfully applied to the trace determination of DNA isolated from Amaryllidaceae plant, namely *Narcissus tazetta* sp. *tazetta*.

This work was supported by the Research Fund of Yuzuncu Yil University, Van, Turkey (Project number: 2007-FED-B44).

PP181**DIFFERENT PLOTS OF SIGNAL vs. TEMPERATURE FOR dsDNA DENATURATION PROCESS IN VOLTAMMETRY AND SPECTROSCOPY****EWELINA ZABOST, ANNA MARIA NOWICKA, MIKOLAJ DONTEN*, and ZBIGNIEW STOJEK***Department of Chemistry, Warsaw University, ul. Pasteura 1, PL 02-093 Warsaw, Poland
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In this work we report on significant changes that occur in current intensity vs. temperature obtained during dsDNA electrooxidation process. Apparently and thermal denaturation proceed in seen earlier (25–50 °C) in voltammetry compared to the absorbance changes (50–85 °C).

Calf thymus double stranded DNA (dsDNA) was investigated in temperature range from 5 to 100 °C. All measurements were done directly without preaccumulation of dsDNA at the electrode surface and without using any mediator¹. dsDNA was dissolved in phosphate buffer solution (pH 7.4). Square wave voltammetry, cyclic voltammetry, chronoamperometry and UV spectroscopy were used. In spectroelectrochemical analysis the electrochemical methods were combined with *on line* UV spectroscopy. Glassy carbon- and carbon mesh electrodes were employed in our studies. Specially designed thermal circuit was applied to spectroelectrochemical and spectroscopic measurements.

To monitor the current changes in the dsDNA thermal denaturation process two separated voltammetric signals of guanine and adenine, which correspond to electrochemical oxidation of these bases, were used. It was found that both signals really increase during thermal denaturation of dsDNA, in the range 25 to 50 °C.

In the same temperature region only a small change in absorbance could be seen. Absorbance intensity does change significantly in the adjacent temperature range of 50–85 °C. Spectroelectrochemical measurements showed that even during the electrooxidation process, there was no essential changes in the absorbance in the temperature range 25 to 50 °C. In terms of electrochemical examination the thermal denaturation process appears to be quite reversible.

Our results do not agree with the results of V. Brabec². He showed that the currents and absorbance intensity obtained during the thermal denaturation process give similar results. However, the electrochemical experiments done by Brabec with dsDNA accumulated at the electrode surface. Dissolved dsDNA might have more possibilities for structural and conformational changes. First, losing the hydrogen bonds and the stacking interactions may be detectable by voltammetry. Second, voltammetry can be more sensitive to the changes that lead to improved charge transport within dsDNA strand³.

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PP182**ELECTRODEPOSITION OF THIN LAYERS OF BIRNESSITE: OPTIMIZATION AND APPLICATION****MANEL ZAIED^a, SOPHIE PEULON^{a,b}, NIZAR BELLAKHAL^a, and ANNIE CHAUSSE^b**^a *Laboratoire de Chimie Analytique et d'Electrochimie, Faculté des Sciences, Campus Universitaire, 2092 Tunis,*^b *UMR 8587 (CNRS-CEA-Université d'Evry), LAMBE, Boulevard François Mitterrand, 91 025 Evry, France sophie.peulon@univ-evry.fr*

Birnessite is the major manganese mineral phase in environment¹. Associated with a very open layered structure, it undergoes cation-exchange reactions and exhibits the largest adsorption capacity on heavy metals than others manganese compounds². Furthermore, Birnessite-type compounds readily participate in oxidation-reduction reactions via a surface mechanism and can react with organic or inorganic compounds³.

Very few studies report the synthesis of birnessite-type compounds as thin films. However, layers directly deposited on current collectors are attractive and can present potential applications in various fields as hazardous waste remediation or chemical sensors⁴.

That is why, previously⁵, we have searched the conditions to electrodeposit thin layers of pure Birnessite onto SnO₂, a cheap transparent semiconductor. Now, we optimized the electrodeposition by studying the influence of various parameters as concentration of manganese salt, pH, potential, temperature. In parallel, thin layers were also characterized by XRD and FT-IR for confirming the nature of the compound electrodeposited onto SnO₂. From these results, some samples were used for studying interactions as illustration of their potential applications.

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PP183**ELECTROANALYSIS OF ADENINE DERIVATES AT GLASSY CARBON ELECTRODE USING FLOW INJECTION ANALYSIS AND LIQUID CHROMATOGRAPHY****ONDREJ ZITKA^{a,b}, FILIP DUSA^{a,b}, DALIBOR HUSKA^{a,c}, VOJTECH ADAM^{a,d}, LIBUSE TRNKOVA^c, FRANTISEK JELEN^f, and RENE KIZEK^{a,*}**^a *Department of Chemistry and Biochemistry,* ^c *Department of Plant Biology,* and ^d *Department of Animal Nutrition and**Forage Production, Faculty of Agronomy, Mendel University of Agriculture and Forestry, Zemedelska 1, CZ-613 00 Brno, Czech Republic,* ^b *Department of Biochemistry, and* ^e *Department of Chemistry, Faculty of Science, Masaryk University, Kamenice 5, CZ-625 00 Brno, Czech Republic* ^f *Laboratory of Biophysical Chemistry and Molecular Oncology, Institute of Biophysics, Academy of Sciences of the Czech Republic, Kralovopolska 135, CZ-612 65 Brno, Czech Republic kizek@sci.muni.cz*

Nucleic acid bases as well as RNA and DNA belong to the most studied molecules. The research of these molecules can be considered as multidisciplinary and, thus, demands cooperation of various branches as analytical chemistry, biochemistry, molecular biology, physics, and others. In the present work we focused on study of basic behaviour of adenine and its derivatives (adenosine, S-adenosyl-L-methionin, 6-benzyl aminopurine, adenosine monophosphate) in flow system. To measure the target molecules we employed flow injection analysis coupled with electrochemical (CoulchemIII) and UV-VIS detector. Primarily we studied the influence of pHs of Britton Robinson buffer on the responses of adenine and its derivatives. The most suitable pH value for determination of the target molecules was 2. Further we measured the dependence of current responses on working electrode potential (hydrodynamic voltammograms). It clearly follows that the optimal working electrode potential was 900 mV. Under the optimized conditions we attempted to determine all target molecules simultaneously. Due to very long time of analysis (more than 40 minutes) we had to mix Britton Robinson buffer with ACN (99:1, %, v/v). We shortened time analysis up to 7 minutes with detection limits below 1 µM.

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PP184**HIGH RESOLUTION VOLTAMMETRIC TECHNIQUES: APPLICATION FOR DIRECT SIMULTANEOUS SPECIES DETERMINATION****ROUMEN ZLATEV*, MARGARITA STOYTCHIEVA, BENJAMIN VALDEZ, JOSE ADOLFO VALERA, and JEAN-PIERRE MAGNIN***Engineering Institute, UABC, Blvd. Benito Juárez s/n, 21280 Mexicali BC, México roumen_zlatev@yahoo.com*The peak overlapping due to the small $E_{1/2}$ difference or

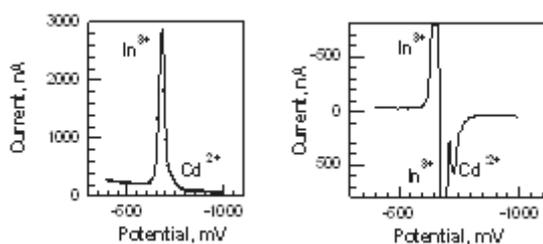


Fig. 1. DPP (left) and DAPV (right) voltammograms of In³⁺ and Cd²⁺ at concentration ratio 40:1 ($\Delta E_{1/2} = 38$ mV)

high concentration ratio or both makes the direct multicomponent trace level voltammetric determinations complicated without preliminary analyte extraction. Employing of some of the second order voltammetric techniques such as RFP¹, DFRP², Second Harmonic AC³ yields distinguished peaks placed on the both side of the zero line even if complete peaks overlapping occurs on the first order voltammetric techniques curves. In spite of their obvious advantages the second order techniques however did not find a wide application because of the complicated equipment needed and problems caused by the high frequency used.

A simple approach applied by the authors recently⁴ employing single couples of rectangular alternative polarity pulses combined with an appropriate signal processing yields a true second order voltammetric technique DAPV, providing higher resolution than the conventional first order techniques such as DPP (Fig. 1) and even than the other second order techniques, providing the same sensitivity as DPP.

The applications of this approach to various potential-time waveforms and the comparison of their resolution power and sensitivity is the subject of the present work. Results obtained with couples of species with small $E_{1/2}$ difference such as In(III)/Cd(II) and Pb(II)/Tl(I) at a wide range of concentration ratios will be presented.

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