



Hendrik Emons and Peter Ostapczuk (Editors)

Electroanalysis



Abstracts

Rheinische-Friedrich-Wilhelms-Universität Bonn



Forschungszentrum Jülich GmbH
Institut für Chemie und Dynamik der Geosphäre
Institut 7: Angewandte Physikalische Chemie

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Electroanalysis

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8th International Conference
held from 11 to 15 June 2000
at the University of Bonn, Germany.

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FOREWORD

For the eighth time, the International Conference on ElectroAnalysis (ESEAC) welcomes participants from all over the world. It is not only the first time that Germany with its long tradition in electrochemistry and analytical chemistry is hosting this conference but it is also the first meeting of this series to be organized in cooperation with the Society of Electroanalytical Chemistry (SEAC). Because of the special year we invited colleagues to present plenary "name" lectures as a bridge between the past and future in our field. It was difficult to select just six electroanalytical chemists from among the many eminent scientists of the last 30 years. But we chose R.N. Adams, I.M. Kolthoff, V.G. Levich, H.-W. Nürnberg, G.J. Patriarche and W. Simon as the subjects of the lectures because of their significant contributions both to the development of the armoury of electroanalytical techniques as well as to expanding their field of application. Moreover, they strongly promoted the teaching of electroanalysis and the establishment of "electroanalytical schools" in their countries. Nowadays, electroanalysis is driven by problem-oriented as well as method-oriented developments. Despite all temporary or regional ups and downs in the academic and public standing of analytical sciences, I am convinced of a bright future for our field. New demands and challenges in life sciences and material sciences - from high spatial resolution at the molecular level to the design of microdevices for high throughput screening - are not only on the horizon but already on some of our lab benches.

The scientific contributions summarized in this book represent an excellent basis for very stimulating discussions during ESEAC 2000 and afterwards, for continuing joint research activities and for establishing new networks of electroanalytical groups all over the world. We would like to thank all colleagues and coworkers who have contributed to the preparation of the conference ESEAC 2000 and this book of abstracts.



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Contents

Plenary Lectures

PL 1	<u>R.M. Murray</u>	<i>The I.M. Kolthoff Lecture:</i> Golden Nanoparticles
PL 2	<u>P.N. Bartlett</u>	<i>The G.J. Patriarche Lecture:</i> The Molecular Design of Electrode Surfaces
PL 3	<u>R.M. Wightman</u>	<i>The R.N. Adams Lecture:</i> True Microanalytical Chemistry: In Situ Observations of Neurotransmitters in Action
PL 4	<u>K. Cammann</u>	<i>The W. Simon Lecture:</i> From ISE towards VISE
PL 5	<u>A.G. Ewing</u>	<i>The V.G. Levich Lecture:</i> Electrochemistry in Ultrasmall Environments: Cells, Nanovials, and Microfabricated Devices
PL 6	<u>J. Buffle</u> , M.-L. Tercier-Waeber, M. Koudelka-Hep	<i>The H.-W. Nürnberg Lecture:</i> Voltammetry in Aquatic Systems: Past, Present and Future

Oral Contributions

OC 1	Ch. Amatore, S. Szunerits, <u>L. Thouin</u> , J.S. Warkocz	In-situ Monitoring of Concentration Profiles by Chronoamperometry Using an Ultramicroelectrode Probe
OC 2	<u>G. Wittstock</u>	Manipulation and Characterization of Microscopic Biochemically Active Regions by Scanning Electrochemical Microscopy
OC 3	<u>S. Daniele</u> , C. Bragato, M.A. Baldo	Use of SECM as a Tool for Amperometric Detection in Thin-Layer Chromatography
OC 4	I. Turyan, M. Atia, D. Burshtain, <u>D. Mandler</u>	Development of Selective Electrodes for Heavy Metals Using Self-Assembled Monolayers and Thin Polymeric Films
OC 5	<u>J.W. Schultze</u> , M. Küpper, E. Klausmann, N. Müller	Electroanalysis in Dynamic Microsystems with High Local Resolution



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is the name of a family of computer controlled electrochemical instruments. Within this family a large number of *different* instruments is available. Thanks to the *modular* concept, every instrument can be configured to the *needs* of the user.

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FI20 A Filter and Integrator module.

ADC750 A fast sampling module.

SCAN-GEN An analog sweep generator.

BSTR10A/20A A current booster for 10 A or even 20A.

BIPOT

pX For pH and bi-potentiometric.

ECN For electrochemical noise measurements.

ECD A low current amplifier.

MUX The multiplexing module.

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This is a non-modular, compact potentiostat/galvanostat capable of measuring or applying a maximum current of 80 mA and with a current resolution of 30 fA. In combination with the GPES software, a large number of electro-chemical techniques can be used, from standard cyclic voltammetry to AC voltammetry and constant current potentiometric stripping analysis.

The instrument has a built in analog integrator, making it possible to do chrono-coulometry, as well as an analog input to measure an external (voltage) signal and output to control a Rotating Disk Electrode.

In combination with a so called IME interface, mercury electrodes can be attached and controlled from the software. This instrument is well suited for all low current applications in case no additional modules are required.

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This instrument in combination with one of the Autolab potentiostats, gives the possibility to do Electrochemical Surface Plasmon Resonance. This technique, which is especially used in pharmaceutical and biochemical research, is used to follow surface processes that take place on a (Au) thin film electrode. Well known is the use to study antibody-antigen interactions. More examples of the use of this technique as well as a more detailed explanation and specifications can be found in the Autolab application note on this subject.

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A modular low-current, low noise potentiostat/galvanostat capable of measuring or applying a maximum current of 250 mA, with a compliance voltage of 12 V and the possibility to do iR-compensation. The instrument basically offers the same possibilities as the μ Autolab II, except for the built in Integrator, which is not present in the Autolab PGSTAT12. In combination with one or more of the optional modules, the instrument can be used for any kind of electrochemical research.

All the optional modules, except the BSTR10A/20A, are available for the PGSTAT12. The instrument can operate in three and four electrode mode.

Autolab/PGSTAT30

This is a modular high current potentiostat/galvanostat with a maximum current of 1 A, a compliance voltage of 30 V and the possibility to do iR-compensation. The instrument offers the same capabilities as the PGSTAT12, but has a bandwidth of over 1 MHz and is, in combination with the FRA2 module, especially dedicated to do Impedance Spectroscopy.

The PGSTAT30/FRA2 system is capable of measuring impedances in the range from 1 mOhm up to 100 GOhm and capacitances from 0.1 pF up to 5000 F and can be used in fields like corrosion research, bio-electrochemistry, battery and super-capacitor research and many other areas.

Another possible configuration is the PGSTAT30 with BSTR10A or BSTR20A for experiments at high currents (10A and 20A respectively).

This configuration also operates in combination with the FRA2.

Of course all the other modules are available for the PGSTAT30 as well. The PGSTAT30 can operate in four electrode (for liquid-liquid measurements for example) as well as in three electrode mode.

Autolab/PGSTAT100

This is a modular high voltage potentiostat/galvanostat capable of measuring or applying a maximum current of 250 mA, a compliance voltage of 100 V and the possibility to do iR-compensation. The instrument offers the same possibilities as the PGSTAT12 and PGSTAT30 and is especially suited for experiments in electrolytes with low conductivity.

All optional modules (except the MUX) are available for the Autolab/PGSTAT100.

- OC 6 A. Walcarius **Electroanalysis with Silica-Modified Electrodes**
- OC 7 C.M.A. Brett, L. Angnes, H.-D. Liess **Carbon Film Electrodes and Application in Electroanalysis**
- OC 8 M. Darder, E. Casero, F. Pariente, L. Hernández, E. Lorenzo **Biosensors Based on Membrane-Bound Enzymes Immobilized in a Membrane Mimetic Layer on Gold Electrodes**
- OC 9 K. Aoki, T. Lei **Electrochemical Detection of Large Single Particles**
- OC 10 A.C. Michael, N.V. Kulagina, J. Cui **Electroanalysis in the Extracellular Space of the Brain with Enzyme-Modified Carbon Fiber Microelectrodes**
- OC 11 J. Schumacher, H.-J. Hecht, U. Dengler, J. Reichelt, U. Bilitewski **Direct Electron Transfer Observed for Peroxidase to Screen-printed Graphite Electrodes**
- OC 12 J. Wang **Controlled Electrochemical Release of DNA and DNA/Lipid Complexes**
- OC 13 B. Deore, Z. Chen, T. Nagaoka **Potential-Induced Enantioselective Uptake of Amino Acid into Molecularly-Imprinted Overoxidized Polypyrrole**
- OC 14 J. Bobacka, J. Nordman, K. Rissanen, A. Lewenstam, A. Ivaska **All-solid-state Ag⁺-ISE based on [2,2,2]p,p,p-cyclophane**
- OC 15 B. Ballesteros Katemann, K. Habermüller, Ch. Kurzawa, A. Hengstenberg, W. Schuhmann **Lateral Deposition of Enzyme-Containing Polymers as a Basis for Miniaturised Amperometric Biosensors**
- OC 16 W. R. Heineman, M. Maizels, M. Stegemiller, J. Divirgilio-Thomas, S. Ross, M. Wanamaker, M. Clager, A. Slaterbeck, Y. Shi, L. Gao, T. H. Ridgway, C. J. Seliskar **Combining Electrochemistry and Spectroscopy into a Single Sensor**
- OC 17 S.J. Woltman, E. Sahlin, W.R. Even, S.G. Weber **Electrochemical Detection by Luminescence Following Electron Transfer**
- OC 18 M.J. Schöning, Yu. G. Mourzina, J. Schubert, W. Zander, A. Legin, Y. Vlasov, H. Lütth **Pulsed Laser Deposition – An Innovative Technique for Preparing Inorganic Thin Film Sensors**



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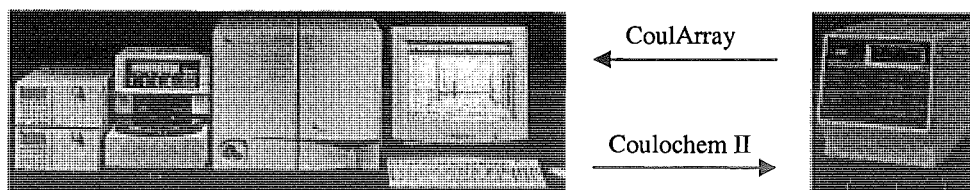
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The company was founded in 1995 and is fully independent. Our principal field of activity is specialized detection methods and separation media for liquid chromatography (HPLC).

Electrochemical detection after separation is no longer confined just to the classical area of neurochemistry. Increased importance has been gained in many other areas such as the food and beverages industries, pharmacology and toxicology, environmental chemistry and, above all, in the pharmaceutical industry. This is due to the excellent sensitivity and selectivity provided by coulometric cells at high working potentials. The unique array technology of the CoulArray® from ESA, Inc. combines these characteristics in an instrument that is unrivalled by any conventional HPLC detector. In view of its much lower price and ease of operation, CoulArray® is a realistic alternative to MS.



For less complex samples the Coulochem II from ESA, Inc. offers similar sensitivity. Both detectors function coulometrically, a major advantage when compared with classical amperometric detection. The Coulochem II can be operated with a variety of cells incorporating electrodes constructed of different materials, for example gold, silver or platinum, thus making it suitable for the analysis of many types of samples.

Additionally, we offer other speciality products including an evaporative light scattering detector (ELSD) and separation media based on methacrylate monoliths which dispense with the problems associated with silica-based materials. In the coming months we hope to introduce the first commercially available FTIR detector for HPLC and GC.

- OC 19 K. Grennan, A. J. Killard,
M.R. Smyth A Single-Step Immunosensor Based on Electrochemical Flow-Injection Analysis for the Real-Time Monitoring of Biospecific Interactions: Applications in Environmental Analysis
- OC 20 F.-M. Matysik Exploitation of Non-Aqueous Electrochemistry for Separation Science
- OC 21 H. B. Mark, Jr., O. Ceylan,
Th. Gbatu, K. Sutton, J.F. Robinson,
J. A. Caruso, A. Galal Solid Phase Microextraction of Anions of Environmental Interest: Applications of Conducting Polymer Microfiber Electrodes for Injection System for HPLC and EIA
- OC 22 E. Beinrohr In-Electrode Coulometric Titrations: Determination of Non-Metals
- OC 23 C.M.G. van den Berg, B. Lange,
M. Ellwood Recent Advances in Catalytic Cathodic Stripping Voltammetry: Selenium, and the Chemical Speciation of Cobalt
- OC 24 S. O. Engblom, J. C. Myland,
K.B. Oldham AC Voltammetry with Applied Alternating Potential of any Amplitude
- OC 25 P. Ugo, L. M. Moretto, J. Chevalet Electroanalysis at Nanomolar and Subnanomolar Concentration Levels by Multiple Square Wave Voltammetry at Ion-Exchanger Coated Electrodes
- OC 26 J. Gadomska, Z. Stojek Voltammetric Analysis of Undiluted Organic Liquids
- OC 27 F. Scholz, Š. Komorsky-Lovric,
M. Lovric A New Access to Gibbs Free Energies of Transfer of Ions Across Liquid-Liquid Interfaces and a New Method to Study Electrochemical Processes at Well-defined Three-Phase Junctions
- OC 28 C. Xhoffer, H. Dillen Electrochemistry: A Powerful Analytical Tool in Steel Research
- OC 29 G. Trettenhahn Qualitative and Quantitative Analysis of Reaction Products on Lead-Sulphuric-Acid Battery Electrodes by Combination of Electrochemical and Infrared Spectroscopic Techniques
- OC 30 H.C. Budnikov, G.A. Evtugyn Environmental Monitoring: Disposable Biosensors or Replaceable Membranes?

BELLTEC Ing. Büro Glocke was founded in 1993 and provides service and distribution of equipment from well-known producers in the following areas:

- electrochemistry
- signal analysis
- registration of measuring data.

In the field of electrochemistry BELLTEC is the representative of Solartron Ltd and AMEL srl. with the products:

- potentiostats/galvanostats
- impedance measuring systems
- sequence analyzers
- dielectric measuring systems
- cryostatic systems
- battery testing systems
- gas mixing and supply systems
- polarographs
- pH meters
- conductivity meters
- cells and electrodes

At ESEAC2000 BELLTAC will present two new products from Solartron Ltd.:

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This system from Solartron has 8 parallel test channels and up to 12 equipments can be controlled by one PC. Each channel can be programmed individually and can provide constant potential, constant current or constant power up to 10 V or 4 A. With two A/D converters one can register simultaneously potential and current at a sampling rate up to 10000 points/s (max. resolution 3 μ V/1.5 nA).

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- OC 31** B. Benito, S. Jiménez, B. Serra,
A.J. Reviejo, J.M. Pingarrón **Graphite-Teflon-HRP Composite Electrochemical Biosensors for the Screening of Phenolic Compounds**
- OC 32** J. Barek, A. Muck, V. Quaiserová,
J. Zima **Polarographic and Voltammetric Determination of Carcinogenic Nitro and Amino Derivatives of Polycyclic Aromatic Hydrocarbons**
- OC 33** P. Jacquinet, R. Knake, P.C. Hauser **Highly Sensitive Amperometric Gas Sensors based on Metallized Ion-Exchange Membranes**

Poster Session A

A 01	J. Bobacka, K. Mikhelson, M. Vazquez, A. Ivaska, A. Lewenstam	Determination of ions in wood pupp by ISEs
A 02	A. Poghosian, P. Schroth, A. Steffen, P. Tobias, H. Lüth, M.J. Schöning	Differential EnFET-based sensor chip with high stability in the long term
A 03	M. Benamor, V.V. Kuznetsov	Potentiometric study of the complexation of ions of barium, zinc and lead with isomeric naphthalene sulfonate ions in aqueous acetone solutions
A 04	N.V. Shvedene, N.N. Leyzerovich, Y. N. Blikova, L. G. Tomilova, I. V. Pletnev	Phthalocyanates of aluminium (III), tin(IV) and copper(II) as active components in salicylate-selective electrodes
A 05	W. Ciesielski, A. Krenc	Potentiometric and coulometric determination of thiols
A 06	J.M. Antelo, A.M. Ferreira, A. Folgueira, S. Fiol, F. Arce	Potentiometric determination of thermodynamic ionization constants of 5,5-dimethylhydantoin and 1-hydroxi 5,5-dimethylhydantoin
A 07	A.J.G. de Mendonca, M. Margarida Vaz, M.I.A. Ferra	Potentiometric determination of Pitzer parameters for sodium benzoate at 298.15 K
A 08	A.A. Karyakin, M. Vuki, L.V. Lukachova, E.E. Karyakina, A.V. Orlov, G.P. Karpacheva, J. Wang	Processible polyaniline as an advanced potentiometric pH transducer for biosensor applications
A 09	K.N. Mikhelson, J. Bobacka, A. Lewenstam, A. Ivaska	Potentiometric performance and interfacial kinetics of neutral ionophore based ISE membranes before and after a contact with primary ions
A 10	T. Yoshinobu, A. Poghosian, H. Ecken, A. Simonis, H. Iwasaki, H. Lüth, M. J. Schöning	Constant-current-mode LAPS for detection of penicillin
A 11	J. Hrdlicka, R. Volf, L. Placek, T.V. Shishkanova, V. Král, A.C. Try, J.L. Sessler	Electropolymerized film based on 2,3-dipyrrol-2'YL-5-aminoquinoxalines as novel sensor for anion recognition

A 12	<u>S.Z. Bathaie</u> , A.A. Moosavi-Movahedi, H. Gharibi, A.A. Ziaee, A.A. Saboury	Investigation of the hydrophobic effect in DNA-surfactant interaction by ion selective membrane electrode
A 13	<u>N.V. Bayanova</u> , A.A. Belyustin, V.V. Derij, I.S. Ivanovskaya, I.V. Murin, A.A. Pronkin, I.A. Sokolov	Lithium ion selective glass electrodes
A 14	A.A. Belyustin	The development of glass electrode theory by B.P. Nicolsky and his school (to the 100th anniversary of B.P. Nicolsky)
A 15	V. Chebotarev, V. Chigirintsev, L. Scherbakova, B. Petrov, Y. Iljina, N. Vaigant, N. Nevskaya, U. Kraev, A. Mosunova, N. Vyatkina	Prediction potentialities and practical use of dithiophosphoric acid high-molecular derivatives in potentiometric titration of nickel, cobalt and zinc
A 16	<u>A.V. Kaverin</u> , A.M. Pisarevsky, I.P. Polozova	Selective redoxmetry for oxidant's analyses (active chlorine, ozone, hydrogen peroxide, molecular oxygen).
A 17	V.K. Chebotarev, B.I. Petrov, L.V. Scherbakova, Ye.G. Iljina, M.V. Ageeva	Potentiometric determination of selenium(IV) and tellurium(IV) by sulfur-containing derivates of pyrazolone.
A 18	V.L.Cherginets, T.P.Rebrova	Potentiometric studies of cation – oxide ion interactions in chloride melts of different acidities
A 19	<u>A.I. Kulapin</u> , T.V. Arinushkina	Solid-state potentiometric sensors for the distinct determination of different type synthetic surfactants
A 20	<u>A. Legin</u> , L. Lvova , A. Smirnova, Yu. Vlasov	PVC “blank” membranes for chemical sensor arrays of “electronic tongue”
A 21	V.K. Chebotarev, L.V. Scherbakova, B.I. Petrov, Y.G. Iljina, M.V. Ageeva	Potentiometric determination of sulfide forming metals ions by antipyrildithiooxamine.
A 22	<u>E.G. Kulapina</u> , R.K. Chernova, E.A. Materova	Forecasting of membrane selective properties using chemical and electrochemical parameters
A 23	<u>M.F. Mousavi</u> , M. Barzegar, S. Sahari	Capric acid as a new ionophore for a lead (II) ion-selective membrane electrode sensor

A 24	<u>E.G. Kulapina</u> , S.A. Mtirokhina, L.V. Apukhtina	Physicochemical characteristics of compounds metal-polyetoxylate-tetraphenilborate: electroanalytical and transport properties of membranes based on
A 25	<u>A. Legin</u> , A. Rudnitskaya, P. Natalenko, B. Seleznev, Y. Vlasov	A study of the sensitivity of chemical sensors to organic substances in solutions
A 26	M. Arvand, M.A. Zanjanchi, <u>M. F. Mousavi</u>	Al-selective membrane electrode based on furil
A 27	A. Legin, <u>A. Rudnitskaya</u> , Yu. Vlasov, A. D'Amico, C. Di Natale	Potentiometric measurements without reference electrode using a sensor system of "electronic tongue"
A 28	<u>A. Smirnova</u> , Y.G. Vlasov, A. Schwake, K. Cammann	Potentiometric properties of anion-selective PVC membranes containing two ion-exchangers with oppositely charged sites
A 29	<u>N.F. Starodub</u> , S.P. Ivashkevich, V.M. Starodub, A.V. Rebriev	ISFET based biosensor for triacylglycerides
A 30	<u>M.F. Mousavi</u> , M. Barzegar, A. Rahmani, M. Shamsipur, H. Sharghi	Pb(II)-selective membrane electrode based on recently synthesized 1,4-bis(propo-2-enyloxy)-9,10-anthraquinone
A 31	<u>T.V. Shishkanova</u> , R. Volf, V. Král, A. Andrievsky, J.L. Sessler	SAPPHYRIN – based Ion-selective electrodes for recognition of dicarboxylate anions
A 32	<u>O.V. Yagodina</u> , E.B. Nikolskaya	Drug investigation by the monoamine oxidase biosensor
A 33	<u>M. F. Mousavi</u> , H. Karami	Dodecyl benzene sulfonate ion-selective electrode based on polyaniline-coated platinum modified electrode
A 34	<u>V.M. Starodub</u> , N.F. Starodub, T.L. Dibrova, B.B. Dzantiev, A.V. Zherdev	Electrochemical control of pesticide level by immune sensor based on the ISFET
A 35	<u>O.V. Yagodina</u> , E.B. Nikolskaya	New potentiometric biosensors for amine determination

Poster Session B

B 01	E. Koglin	In situ analysis of cationic surfactants on silver electrode surfaces by SERS microprobe spectroscopy
B 02	<u>C.A. Wijayawardhana</u> , G. Wittstock, H.B. Halsall, W.R. Heineman	Microscopic immunomagnetic bead domains and detection by scanning electrochemical microscopy in electrochemical immunoassay
B 03	<u>O. Köster</u> , W. Schuhmann, H. Vogt, W. Mokwa	On the determination of standard rate constants using ultra-microelectrode arrays and electrochemical impedance spectroscopy at low frequencies
B 04	J. Pei, M.-L. Tercier-Waeber, J. Buffle, G.C. Fiaccabrino, M. Koudelka-Hep	Individually addressable gel-integrated microelectrode arrays for high resolution of the trace metal concentration profile measurements at liquid-liquid and liquid-solid Interfaces
B 05	<u>A. Beckmann</u> , B.A. Coles, R.G. Compton, P. Gründler, F. Marken, A. Neudeck	Coupled heat and mass transport at a directly and continuously heated wire
B 06	<u>M. Mosbach</u> , T. Laurell, J. Nilsson, E. Csöregi, W. Schuhmann	Determination of diffusion coefficients of electroactive species by means of microelectrochemical "time-of-flight" experiments
B 07	<u>B. Ballesteros Katemann</u> , W. Schuhmann	Scanning electrochemical microscopy with improved resolution. constant-distance control and surface-tilt compensation
B 08	<u>M. Antonietta Baldo</u> , S. Daniele, C. Bragato, G.A. Mazzocchin	Amperometric determination of the total acidity of distilled spirits with platinum microelectrodes
B 09	<u>A. Lynch</u> , D. Diamond	The development of a one-step diagnostic system for cystic fibrosis (CF) using a potentiometric microelectrode sensor array
B 10	F.-J. Pérez-Alonso, L. Agüí, P. Yáñez-Sedeño, <u>J.M. Pingarrón</u>	Determination of additives and monomers in styrene and styrene-based polymers using cylindrical microelectrodes
B 11	<u>M. Perdicakis</u> , N. Grosselin, J. Bessière	Electrochemical behaviour of potassium ferrocyanide at single micrometric particles of Platinum. Comparison with an ultramicroelectrode

B 12	A. Baade, A. Poghosian, <u>H. Emons</u>	Analytical procedures for the electrochemical determination of heavy metals and hydronium ions in microvolumes of natural water
B 13	<u>L.M. Moretto</u> , P. Ugo, B. Brunetti, C.R. Martin, J.Chevalet	Electroanalysis with nanoelectrodes ensembles
B 14	<u>M. Palys</u> , Z. Stojek	Effect of supporting electrolyte deficiency in voltammetric determination of equilibrium constants
B 15	<u>B. Hüllenkremer</u> , O. Glück, H. Emons, M.J. Schöning	Exploitation of voltammetry for the trace analysis of metals
B 16	I. Ait Arkoub, C. Amatore, <u>C. Sella</u> , L. Thouin, J.S. Warkocz	Electrochemical behaviour of a Nafion®-coated double band microelectrode loaded with ferric cations
B 17	R. Ramaraj, C. Kabbe, F. Scholz	Electrochemistry of microparticles of tris(2,2'-bipyridine)ruthenium(II) hexafluorophosphate
B 18	C. Amatore, <u>S. Szunerits</u> , L. Thouin	Mapping concentration profiles within a steady state diffusion layer using an ultramicroelectrode

Poster Session C

C 01	<u>D.W.M. Arrigan</u> , T. Iqbal, L. Le Bihan, M. Pickup	Studies of organosulfur films on gold electrodes for metal ion detection
C 02	S. Ernst, <u>H. Baltruschat</u> , I. Vogel	Detection of hydrocarbons in air by adsorption on Pt-electrodes using a modified anodic stripping procedure
C 03	<u>M. Fojta</u> , T. Kubicarova, L. Havran, E. Palecek	Mercury electrodes modified with supercoiled DNA: electrochemical probes of DNA interactions and damage
C 04	M. Etienne, <u>A. Walcarius</u> , J. Bessiere	Voltammetric detection of heavy metals after accumulation on polysiloxane-immobilized amine ligands
C 05	<u>B. Ballarin</u> , M. Berrettoni, M. Morigi, E. Scavetta, R. Seeber, D. Tonelli	Oxidative electrocatalytic determination of organic and inorganic substrates at electrodes modified with nickel-based hydrotalcites
C 06	<u>F. Björefors</u> , B. Liedberg	Characterization of the capacitance and quality of thiol based self assembled monolayers by impedance spectroscopy and cyclic voltammetry
C 07	B. Filanovsky, T. Bourenko	Some nitrides of transitional metals as new material for chemical sensors
C 08	<u>J.C. Hoogvliet</u> , M. Dijkma, B. Kamp, W.P. van Bennekom	EQCM as a tool to characterize self-assembled monolayers of thioctic acid on gold
C 09	<u>G.-U. Flechsig</u> , O. Korbut, P. Gründler, M. Jasinski, J. Wang	Electrically heated biosensors
C 10	<u>S.B. Hočevar</u> , J. Wang, L. Chen, B. Ogorevc	One-step electropolymeric coimmobilization of glucose oxidase and heparin for amperometric biosensing of glucose
C 11	<u>A. Kurowski</u> , J.W. Schultze	Porous silicon as base material for sensor applications
C 12	<u>H. Ju</u> , Y. Xiao, H. Chen	Electrocatalytic reduction of hemoglobin at toluidine blue/polypyrrole film modified gold electrodes

C 13	<u>C. Kurzawa</u> , A. Hengstenberg, W. Schuhmann	Electrochemically-induced deposition of enzyme-containing films as a basis for the reproducible preparation of amperometric biosensors
C 14	<u>W. Hyk</u> , M. Ciszowska, Z. Stojek	Voltammetric studies of transport of analytes in poly(n-isopropylacrylamide-co-acrylic acid) gels swollen by methanol
C 15	S. Serradilla Razola, J.-C. Viré , <u>J.-M. Kauffmann</u>	Solid carbon paste electrode based on phenothiazine and horse radish peroxidase
C 16	<u>Z. Navrátilová</u> , P. Kula	Sorption of mercury and gold on the montmorillonite modified electrode
C 17	P. Schroth, M.J. Schöning, B. Weißbecker, S. Schütz, H.E. Hummel, H. Lüth	Insect-antenna – FET junction for biochemical sensing
C 18	N. Mano, <u>A. Kuhn</u>	Effect of Ca²⁺ on the electrochemical detection of NADH with nitro-fluorenone modified electrodes
C 19	<u>H. Ju</u> , C. Shen	Electrocatalytic deduction and determination of dissolved oxygen on poly-nile blue modified electrode
C 20	Z. Jusys	Electrochemical quartz crystal microbalance response to poly(vinylferrocene) film redox doping by hexafluorophosphate; Hexafluoroarsenate and hexafluoroantimonate anions
C 21	<u>S. Reiter</u> , K. Habermüller, W. Schuhmann	Reagentless glucose biosensors. evidence for electron-hopping via polymer-bound Os-complexes in an electrochemically deposited redox polymer
C 22	<u>F. Marken</u> , A. Saterlay, K. Holt, C.H. Goeting, J.S. Foord, R.G. Compton	Electroanalysis at boron-doped diamond electrodes
C 23	<u>J. Labuda</u> , M. Bučková, M. Vaničková, A. Ferancová	Chemically modified electrodes with DNA and cyclodextrin
C 24	<u>L.V. Lukachova</u> , I.L. Mattos, A.A. Karyakin, M. Baust-Timpson, L. Gorton	New glucose biosensors based on prussian blue and crystalline, cross linked and lyophilized glucose oxidases: a comparative study

C 25	M.C. Rodriguez, <u>G.A. Rivas</u>	Highly selective amperometric glucose biosensor based on carbon paste modified with copper and glucose oxidase
C 26	L. Campanella, A. Sulpizio, <u>M.P. Sammartino</u> , M. Tomassetti	Cell biosensors able to operate in organic solvent or gaseous medium for the analysis of benzene, preliminary results
C 27	<u>K. Winkler</u> , M.E. Plonska	Electrocatalytic reduction of fullerene C60 at electrodes modified by $[M^{III}(\text{Bipyridine})_3](\text{ClO}_4)_3$ (M = Co and Fe)
C 28	L. Campanella, A. Civita, M.V. Russo, <u>M.P. Sammartino</u> , G. Visco	Voltammetric determination on modified electrodes of active principles in drugs
C 29	M.D. Rubianes, <u>A.G. Rivas</u>	Iridium dispersed enzymatic carbon paste electrode for the quantification of phenols and catechols
C 30	A. Eftekhari	Direct modification of zinc electrode with zinc hexacyanoferrate film
C 31	<u>J.C. Vidal</u> , M.T. Pérez, S. Méndez, J.R. Castillo	Two strategies with third generation organic conducting salt based enzymatic biosensors: electropolymerization over the salt and its entrapment into a sol-gel matrix
C 32	<u>V. Rosca</u> , L. Muresan, C. Cristea, I.A. Silberg, I.C. Popescu	Gold electrodes modified with new phenothiazine derivative: electrochemistry and electrocatalytic oxidation of NADH
C 33	<u>L.N. Balyatinskaya</u> , G.M. Fofanov, S.A. Khorishko	Mercuric-graphite modified electrodes in voltammetrical heavy metals determination
C 34	<u>E.V. Khaldeeva</u> , E.P. Medyantseva, A.E. Shusharina, N.I. Glushko, H.C. Budnikov	Application of kinetic data for optimization of electrochemical immunoassay
C 35	R. Turquini Ferrari, L.M. Saragiotto Colpini, E. Aparecido Toledo, C. Maieru Macedo Costa	Electrochemical catalytic reduction of dioxygen by cobalt(II) hematoporphyrin complex immobilized on silica gel incorporated in carbon-paste electrode
C 36	<u>L. Rotariu</u> , C. Bala, V. Magearu	Soft drinks sucrose determination using a microbial biosensor based on oxygen electrode with electrolyte in non-aqueous medium

C 37	I. Luiz de Mattos, L. Gorton, T. Ruzgas, A.A. Karyakin	Sensor for hydrogen peroxide based on Prussian blue modified electrode: improvement of the operational stability
C 38	A. Eftekhari	Electrochemical properties of mixed iron/cobalt hexacyanoferrate film modified electrode
C 39	E.P. Medyantseva, M.P. Kutyreva, N.Y. Ilyicheva, S.A.Eremin, H.C. Budnikov	An application of cholinesterase amperometric biosensor in environment monitoring of sim-1,3,5-triazine herbicides contamination
C 40	<u>G. Turdean</u> , I.C. Popescu, C. Rosu, A. Narváez, E. Dominguez	Reagentless biosensors based on self-deposited Fe₄(PMo₉)₂ for glucose amperometric detection
C 41	<u>L.G. Shaidarova</u> , A.Y. Fomin, E.P. Medyantseva, H.C. Budnikov	Electrocatalytic activity of carbon paste electrode modified with osmium in cholinesterase enzyme systems
C 42	A. Eftekhari	Electrocatalysis at aluminum electrode modified with manganese hexacyanoferrate(III) film electrode
C 43	N. Ulakhovich, S. Babkina, Y. Zyavkina, E. Moiseeva	Voltammetric determination of DNA effectors using DNA based biosensor

Poster Session D

D 01	J.M. Morgado, <u>C.M.A. Brett</u>	Electrochemical determination of trace metals in ecotoxicological testing
D 02	<u>M. Froning</u> , M. Burow, H. Emons, K. Hoppstock, C. Mohl, M. Rossbach, J.D. Schlodt, H. Schüßeler, B. Süßenbach, P. Ostapczuk	Daily quality assurance by electroanalytical determination of trace elements in environmental samples
D 03	<u>K.-H. Bauer</u> , H.R. Eschnauer	The indirect inversvoltammetric determination of the bismuth complex formation capacity in wine - a method to estimate iron cloudings in wine
D 04	<u>M.C. Antunes</u> , J.E. Simão, A.C. Duarte	Resolution of voltammetric overlapped peaks using chemometrics multivariate calibration methods
D 05	J. Monné, <u>E. Companys</u> , M. Torrent J. Puy, J. Salvador, J. Galceran, J. Cecília, J.L. Garcés, F. Mas	Determination of heterogeneous complexation parameters through voltammetric techniques
D 06	<u>N.A. Diab</u> , A. AbuZuhri, W. Schuhmann	Sequential-injection stripping analysis (SISA) of nifuroxime using DNA-modified glassy carbon electrodes
D 07	B.H. Cruz, <u>M.S. Díaz-Cruz</u> , J.M. Díaz-Cruz, C. Ariño, R. Tauler, M. Esteban	Multivariate curve resolution as a tool for the interpretation of overlapping voltammetric signals
D 08	<u>V. Dorcák</u> , K. Markušová	Determination of heavy metals in fish muscle tissue by differential pulsed anodic stripping voltammetry
D 09	F. Alt, K.-H. Bauer, H.R. Eschnauer, G.R. Scollary	Element traces and ultratraces in wine
D 10	<u>I. Švancara</u> , B. Ogorevc, M. Novič, K. Vyřas	Determination of iodide in table salts containing some anticaking agents using stripping potentiometry with selective sensing at a tricresyl phosphate-based carbon paste electrode
D 11	<u>G.-U. Flechsig</u> , O. Korbut, P. Gründler	Investigation of deposition and stripping phenomena at the heated gold wire electrode in comparison to the rotating disk electrode: copper(II), mercury(II) and arsenic(III)

D 12	<u>R. Petr</u> , Z. Navrátilová	Voltammetry of gold complexes on carbon paste electrode
D 13	A. Schwarz, O. Bagel, H.H. Girault	Electrochemical protein separation and electrochemical protein quantification method
D 14	M.M. Ghoneim, A.M. Hassanein, A. Tawfik	Determination of terfenadine in its dosage forms and human serum by adsorptive stripping voltammetry
D 15	<u>P. Kulová</u> , M. Kotouček	Indirect voltammetric determination of quaternary nitrogenous compounds
D 16	<u>Ø. Mikkelsen</u> , K.H. Schrøder	An oscillating and renewing silver electrode for cadmium and lead detection in differential pulse stripping voltammetry
D 17	<u>I. Švancara</u> , B. Ogorevc, S.B. Hočevár, K. Vytřas	Characterisation and testing of carbon paste-based electrodes for their use in stripping potentiometry
D 18	P. Ostapczuk, M. Froning	Cadmium and lead determination in herbal drugs by potentiometric stripping analysis
D 19	<u>Z. Lukaszewski</u> , J. Chlebicki, E.W. Nowak, A. Szymanski	The effect on alkyl length on the analytical signal of monoalkylethers of butylene oxide – ethylene oxide block copolymers in adsorptive stripping tensammetry
D 20	<u>F. Quentel</u> , C. Elleouet, C. Madec, J. Talarmin	A cathodic stripping square wave voltammetry of the molybdenum-1,10 phenanthroline complex
D 21	<u>H.P.A. Nouws</u> , C. Delerue-Matos, J.L.F.C. Lima	Electrochemical oxidation study of fenvalerate at a glassy carbon electrode. A square wave voltammetric methodology for its determination in environmental water samples
D 22	<u>Z. Lukaszewski</u> , S. Sanocka, A. Szymanski	Analytical signals of the ion pair tetrabutylammonium cation and dodecylbenzenesulphate anion in adsorptive stripping tensammetry
D 23	<u>D. Pechová</u> , M. Kotoucek	Voltammetric determination of 6-benzylaminopurine
D 24	Y.M. Temerk, M.S. Ibrahim, A.M. Kawde	Stripping analysis of 3-methylxanthine and 7-methylxanthine at the charged interface

D 25	<u>B. Van Haute</u> , P. Westbroek, E. Temmerman	Voltammetric study and determination of hydrogen peroxide in aqueous solutions
D 26	E. Khaled, R. Metelka, I. Švancara, <u>K. Vytras</u> , H.N.A. Hassan	Carbon paste electrodes modified with inorganic mercury compounds and their use in potentiometric stripping analysis of heavy metals
D 27	<u>L. Tmková</u> , R. Kizek, O. Dračka	Application of elimination voltammetry to the electroanalysis of an adsorbed substance
D 28	<u>P. Westbroek</u> , E. Temmerman	Sensors for on line measurement of chemical oxygen demand based on rotating ring-disc multipulse voltammetry
D 29	<u>J. Zima</u> , J. Barek	Polarographic and voltammetric determination of selected azo dyes
D 30	E.M. Richter, M.A. Augelli, <u>L. Angnes</u>	Potentiometric stripping analysis of copper using gold electrodes from recordable compact discs
D 31	V.I. Grigoriev, Yu.F. Milyaev, <u>L.N. Balyatinskaya</u> , G.M. Fofanov	A.C. stripping voltammetry heterocycles at trace level with adsorption on mercury hanging drop electrode
D 32	P.N. Linnik	Application of anodic stripping voltammetry to the investigation of the heavy metal complexation in the Dnieper waterbodies
D 33	A. M. Cavicchioli, I.G.R. Gutz	Indirect voltammetric monitoring of the efficiency of the photodegradation of EDTA mediated by TiO ₂ in suspension
D 34	E.A. Leites, N.A. Gluhova, V.V. Suzeva	Cathodic stripping voltammetry determination of dimethylsulfide in condition of complex with mercury (II) chloride
D 35	<u>J.C. Sturm</u> , A. Álvarez-Lueje, <u>L.J. Núñez-Vergara</u> , J.A. Squella	Voltammetric analysis of 1,4-dihydropyridines: application to degradation studies

Poster Session E

E 01	<u>U. Backofen</u> , F.-M. Matysik, C.E. Lunte	Sensitivity and selectivity in non-aqueous capillary electrophoresis with electrochemical detection
E 02	Th. Löffler, Z. Jusys, H. Baltruschat	Characterization and practical test of a new dual thin-layer cell used for combination of DEMS and EQCM
E 03	<u>H.R. Eschnauer</u> , K.-H. Bauer, G. Schwedt	The oenologic monitor cell
E 04	<u>Kh. Brainina</u> , Y. Maksimov, A. Volkonsky, N. Malakhova, L. Kolyadina, L. Miroshnikova, S. Parshakov	Electrochemical pretreatment of water samples in a flow-through discrete stripping voltammetric system
E 05	D. Daniel, <u>I.G.R. Gutz</u>	Long path spectroelectrochemical flow cell with inexpensive gold electrodes
E 06	T. Kappes, B. Galliker, <u>P.C. Hauser</u>	Contactless conductometric and simplified amperometric and potentiometric detection for a portable capillary electrophoresis instrument
E 07	J. Gorecki, <u>J. Golas</u>	Electrochemical procedure for determination of mercury in waste soil samples
E 08	T. Galeano, <u>A. Guiberteau</u> , N. Mora, P. Parrilla, F. Salinas	Rapid and sensitive determination of 4-nitrophenol, 3-methyl-4-nitrophenol, DNOC, parathion-methyl, fenitrothion and parathion-ethyl by liquid chromatography with electrochemical detection
E 09	<u>A. Moehring</u> , M.M. Lohrengel	Preparation of Ir-doped titanium anodes and their investigation by the droplet cell
E 10	<u>J.C. Hoogvliet</u> , M. Dijkma, B. Kamp, W.P. van Bennekom	Electrochemical pretreatment of gold to obtain a reproducible surface for molecular self-assembly
E 11	M. Strasser, T. Kappes, P.C. Hauser, W. Hoffmann	Electrochemical detection in capillary electrophoresis for the analysis of wine
E 12	C.M.N. Azevedo, J. Tramontina, D.S. Azambuja, <u>C.M.S. Piatnicki</u>	Determination of trace level chromium(VI) by flow injection amperometry at gold microelectrodes arrays

E 13	<u>J.A. Rodrigues</u> , A.A. Barros, P.G. Rodrigues	Determination of diacetyl by adsorptive stripping voltammetry under flow conditions at the hanging mercury drop electrode without oxygen removal
E 14	J.L. Costa Lima, C. Delereue-Matos, <u>M. Carmo Vaz</u>	Determination of citric acid in soft drinks using a potentiometric flow injection system
E 15	<u>J.C. Vidal</u> , E. García-Ruiz, J.R. Castillo	Comparison of continuous flow versus flow injection electropolymerization of conduction polypyrrole films in the preparation of glucose biosensors
E 16	<u>L.G. Shaidarova</u> , A.Y. Fomin, S.A. Zaripova, I.M. Fitsev, H.C. Budnikov	Electrocatalytic flow detection of some S- containing compounds on metallophthalocyanine modified electrodes
E 17	C.D. Garcia, <u>P.I. Ortiz</u>	BHT quantification by HPLC with a polymer modified electrode determination
E 18	Z. Wu	Electrochemical detection for capillary electrophoresis with Co-axis disk electrodes

Poster Session F

F 01	T. Langkau, H. Baltruschat	Pressure modulation, a new technique for the electrochemical determination of adsorption and reaction volumes
F 02	<u>F. Berbel</u> , R. Serra, J.M. Díaz-Cruz, C. Ariño, M. Esteban	A polarographic approach to the study of heterogeneity in heavy metal- humic matter systems
F 03	K. Soltyk, A. Lozak, M. Warowna-Grzeskiewicz, <u>Z.E. Fijalek</u>	The AAS, ICP-MS and electrochemical determinations of zinc in selected pharmaceutical preparations
F 04	<u>G. Farsang</u> , T. Dankházi, P. Simon, M. Kádár, and Sz. Pusztai	The voltammetric oxidation of halogenoanilines in acetonitrile solvent
F 05	D. Schwudke, R. Stößer, F. Scholz	Solid-state electrochemical, X-ray and spectroscopic characterization of mixed crystals of iron-copper hexacyanoferrates
F 06	E. Gasana, P. Westbroek, E. Temmerman, H.P. Thun	Determination of diffusion coefficient of sodium dithionite and mechanism of oxidation reaction in alkaline solution
F 07	P. Gründler, D. Degenring	Near critical and super critical fluids in electrochemical sensors
F 08	<u>Z.E. Fijalek</u> , K. Sarna, A. Piwonska	Cyclic voltammetry and quartz crystal microbalance electrochemical studies on thiosalicylic acid and dithiodibenzoic acid
F 09	J.-M. Séquaris	Application of electrochemical methods for the interactions study of some synthetic organic matters with clay minerals
F 10	<u>M. Jasinski</u> , P. Gründler, J. Wang, G.-U. Flechsig, A. Kirbs	Heated mercury film electrodes on iridium and carbon basis
F 11	P. Suchocki, K. Sarna, <u>Z. Fijalek</u>	Analytical investigations of the new organic platinum(IV) derivative
F 12	H. Haupt	Measuring electric resistivity of solid insulating materials by means of low frequency dielectric spectroscopy

F 13	<u>Z. Lukaszewski</u>	Competitive potential of electroanalytical over other methods in surfactant analysis
F 14	<u>H. Kahlert</u> , O. Schäfer, H. Wulff, F. Scholz	Electroanalysis of hydrothermally synthesised Prussian blue
F 15	<u>F. Marken</u> , B.A. Coles, R.G. Compton	Microwave activation of electrochemical processes
F 16	F. Scholz, D. Schwudke, M. Sigmund, A.R. Stößer	The interaction of Prussian blue and dissolved hexacyanoferrate ions with goethite (α-FeOOH) studied to assess the chemical stability and physical mobility of Prussian blue in soils
F 17	A.I. Vorobyova, <u>E.A. Outkina</u>	Chrono-voltamperometry as a method of metal-metal thin film systems investigation
F 18	<u>A. Michelitsch</u> , <u>M. Wurglics</u> , B. Biza, K. Westerhoff, M. Schubert-Zsilavecz, A. Baumeister, W. Likussar	Determination of hypericin in various biological fluids by differential pulse polarography
F 19	J. Tramontina, S.B. Guterres, <u>C.M.S. Piatnicki</u> , D.S. Azambuja	Removal of Cu^{2+} and Cd^{2+} from aqueous solutions onto reticulated vitreous carbon coated electrodes
F 20	B.B. Radojevic, H.P. Buchkremer, A.A. Khanlou, D. Stoeber	Electroanalytical studing of Ni_{51.24}Ti_{48.76} shape memory alloys
F 21	N. Saidi, H. Saidi, B. Saidani, S.P. Stoylov	A conductance electric study of PbO_2 particles in the acid solution of H_2SO_4 with the presence of the electric field
F 22	<u>J. De Strycker</u> , P. Westbroek, E. Temmerman	New observations in hydrogen permeation through palladium membranes
F 23	L. Campanella, T. Ferri, P. Sangiorgio, <u>M.P. Sammartino</u>	Total organic carbon (TOC) analysis by photodegradation based apparatur using nanocrystalline TiO_2 as catalyst
F 24	F. Scholz, S. Schädel, A. Schultz, F. Schauer	Chronopotentiometric study of laccase catalysed oxidation of quinhydrone microcrystals immobilised on a gold electrode surface and of the oxidation of a phenol derivatised graphite electrode surface

F 25	U. Schröder, K.B. Oldham, J.C. Myland, P.J. Mahon, F. Scholz	Modelling of solid-state voltammetry of immobilized microcrystals assuming an initiation of the electrochemical reaction at a three-phase junction
F 26	U. Schröder, F. Scholz	The solid state electrochemistry of metal octacyanomolybdates, octacyanotungstates, and hexacyanoferrates explained on the basis of dissolution and reprecipitation reactions, their lattice structures and crystallinities
F 27	<u>P. Westbrook</u> , E. Temmerman	Reaction path of PbO₂ deposition on a platinum electrode
F 28	M. Mohan Rao, M. Jayalakshmi, O. Schäf, H. Wulff, U. Guth, F. Scholz	The electrochemical behaviour of solid lithium cobaltate (LiCoO₂) and lithium manganate (LiMn₂O₄) in an aqueous electrolyte system
F 29	<u>P. Spitzer</u> , U. Sudmeier	High accuracy conductivity measurements
F 30	<u>I. VanMoortel</u> , J. De Strycke, E. Temmerman, P. Westbrook	Study of the corrosion of molybdenum, tin(IV)oxide, iron and metal alloys in molten enamel
F 31	A.V. Klimenko, <u>I.B. Svir</u> , A.I. Bykh	Computer simulation for the electrochemiluminescent ecological analysis (ecla)
F 32	R.N. Goyal, N. Kumar	Oxidation chemistry and biochemistry of 5-hydroxyindole
F 33	D. Mockutė, R. Butkienė, G. Bernotienė	Investigation of cathodic reaction of saccharin and n-methylsaccharin during nickel electrodeposition in electrolytes containing different anions
F 34	<u>X.M. Pei</u> , D.J. Blackwood	The influence of fluorides on titanium and titanium alloys in simulated oral environments
F 35	I.F. Abdullin, E.N. Turova, H.C. Budnikov	Coulometric evaluation of antioxidant capacity of berry, fruit and vegetable saps
F 36	<u>A. Iona</u> , F.G. Banicab	Voltammetric studies on the catalytic nickel prewave induced by 6-mercaptopurine-9-D-ribose (MPR)
F 37	<u>E.E. Iorgulescu</u> , Ion Tonase	The electrochemical behaviour and electroanalysis of bilirubin at mercury electrodes

F 38	G.D. Levvytska, N.P. Poperechna, L.O. Dubenska	Electrochemical behaviour of eriochrom red B,A N-Geterocyclic Azodye, and ist complexes with rare earth
F 39	<u>S. Litescu</u> , G.-L. Radu, M. Diaconu	Antioxidative power evaluation of some phenolic antioxidants – electroanalytical approach
F 40	E. Galeazzo, W.J. Salcedo, M.O. Perez Lisboa, <u>N. Peixoto</u> , F. J. Jamirez-Fernandez	Virtual instrumentation for multilayered porous silicon formation
F 41	Y.I. Dykhal, <u>E.P. Medyantseva</u> , N.V. Kalacheva, H.K. Budnikov	Catalytic waves of hydrogen in voltammetric control of immunoreactions
F 42	<u>N.F. Starodub</u> , V.V. Il'chenko, V.M. Starodub, I.I. Horajchuk, G.V. Kuznetsov, A.V. Palladin	Application of an electrometrical approach to monitor formation of specific immune complexes on the porous silicon and metal surfaces
F 43	I.A. Vrublevsky, V.M. Parkun	Influence of structural stresses onto kinetics of aluminium anodic oxidation
F 44	Oleg Sklyar, Gunther Wittstock	Applications of the Boundary Element Method for Numerical Simulations in SECM Investigations

PLENARY LECTURES

Dedicated to
Issak M. Kolthoff

born in Almelo, Netherlands, in 1894
died in St. Paul, Minnesota, U.S.A., in 1993

Kolthoff studied chemistry and pharmacy at the State University of Utrecht (The Netherlands) and obtained a Ph.D. from this university in 1918. He was conservator at the Pharmaceutical Institute of the State University of Utrecht (1917-1927) and lecturer in applied electrochemistry (1924-1927). In 1927 he moved to the University of Minnesota (U.S.A.) holding positions as Professor of Analytical Chemistry and Head of the Analytical Division until 1962 when he became Emeritus Professor of Analytical Chemistry.

Kolthoff has been called “the founder of North American electroanalytical chemistry”. He has taught and influenced generations of analytical chemists, wrote many monographs and textbooks. His enormous original contributions to electroanalysis started already during his time in Utrecht and continued for more than half a century. He studied acid-base titrations and introduced buffer solutions. He pioneered conductometric analysis, especially end-point detection, and coined the terms potentiometric and amperometric titration, respectively. Kolthoff studied analytically important precipitates for gravimetric analysis and was a pioneer in using radioactive indicators. He investigated reactions in non-aqueous solvents and developed an industrial method for the low temperature synthesis of rubber during World War II. In 1967 he investigated the analytical application of crown ethers.

THE I.M. KOLTHOFF LECTURE

GOLDEN NANOPARTICLES

Royce W. Murray

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Izaak Maurits Kolthoff (1894-1993) is widely regarded as a principal founder of modern analytical chemistry. His research was exceptionally broad and his >900 publications encompass proton and electron transfers, precipitation, voltammetry, polymerization, catalyzed reactions, and non-aqueous media. Kolthoff's impact was not solely by breadth and productivity, but was based on his recognizing and introducing into analytical chemistry fundamental ideas and concepts that had emerged in other chemistry disciplines. This lecture will introduce some of these connections.

In the second part of the lecture I will discuss work from my own laboratory on ligand-stabilized metal nanoparticles, or monolayer-protected clusters (MPCs) that can be regarded as devolving from Kolthoff's great foundation. Synthesis of MPCs involves a complex nucleation/growth/passivation process that is incompletely understood. Freshly created Au MPCs undergo a "ripening" process in which the average Au core increases in size. After isolation, MPCs can be fractionated by core size and thereby is revealed their property, when dissolved in electrolyte solutions, of undergoing single electron double layer charging. Various manifestations of this quantized double layer characteristic will be described.

This research was supported by grants from the National Science Foundation and the Office of Naval Research.

Dedicated to
Gaston J. Patriarche

born in Obaix-Buzet, Belgium, in 1930
died in Brussels in 1991

Patriarche studied at the Free University of Brussels (ULB), Belgium and became a pharmacist in 1956. Starting his career in 1957 as an assistant he obtained a Ph.D. degree in Pharmaceutical Sciences in 1963 from ULB. He was promoted to Associate Professor in 1969 and Full Professor in 1977 at the Pharmaceutical Institute of ULB.

Patriarche became early interested in electroanalytical techniques and promoted significantly their application in pharmaceutical analysis. His research started with coulometric measurements of metal ions and organic compounds and was expanded to polarography and voltammetry at solid electrodes. He was particularly interested in developing modified electrodes and enzyme-based biosensors for pharmaceutical and biomedical applications. He contributed also to new spectrophotometric and chromatographic methods in pharmaceutical analysis and has authored many publications and book chapters.

THE G.J. PATRIARCHE LECTURE

THE MOLECULAR DESIGN OF ELECTRODE SURFACES

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From the early studies using mercury electrodes through to the more recent developments and commercialisation of biosensors electroanalytical chemistry has had an important role to play in the study and analysis of samples of medical diagnostic, pharmaceutical and biochemical importance. Measurements of this type frequently require the specific detection of complex molecules in complex mixtures and consequently place stringent requirements on the selectivity and specificity of the electrode. Stimulated by this challenge a variety of strategies have been developed over the past 30 years to modify and control the electrode surface at the molecular level and to transduce the molecular interactions between the electrode and the analyte into an analytical signal. These developments have been matched by an increasing sophistication in the *in situ* techniques available to characterise the electrode surface at the molecular level.

In this lecture I want to review these developments in the design and fabrication of modified electrode surfaces starting from the early experiments with amperometric and potentiometric electrodes and coming up to the present day with self assembled structures and multicomponent systems. I also want to review the electroanalytical applications of these modified electrodes and to look forward to try to see what the next 30 years may bring in this area.

Dedicated to
Ralph N. Adams

Ralph N. Adams: Professor Emeritus at the Department of Chemistry, The University of Kansas, Lawrence, KS, U.S.A.

He was born in Atlantic City, New Jersey (U.S.A.) in 1924. Adams received a B.S. degree in chemistry from Rutgers University (1950) and a Ph.D. degree from Princeton University (1953). He remained on the faculty at Princeton from 1953-1955.

Professor Adams joined the staff of the Department of Chemistry at the University of Kansas in 1955. His research interests until 1969 centered on the mechanisms of organic electrode reactions. In 1964 he was a J.S. Guggenheim Fellow in Zuerich, Switzerland. His famous book on "Electrochemistry at Solid Electrodes" was published in 1969.

Afterwards the research interests of his laboratory shifted to applying electrochemistry to the problems of the neurosciences. Adams received fundamental training in neuroanatomy, neurophysiology, clinical psychiatry, etc. and held also a joint appointment in Neurobehavioral Sciences at the Menninger School of Psychiatry in Topeka, Kansas. He was the pioneer of the field of neuroelectrochemistry and has opened new horizons both in problem-oriented and method-oriented electroanalysis.

THE R.N. ADAMS LECTURE**TRUE MICROANALYTICAL CHEMISTRY: IN SITU OBSERVATIONS OF
NEUROTRANSMITTERS IN ACTION**

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Chemical events that are localized to microdomains are often quite important and can have macroscopic consequences. For example, chemical secretion from individual biological cells can dictate the overall behavior of an animal. Since many of the chemical messengers employed by biological cells are readily oxidized, electrochemical techniques are well suited to observe this process, as first recognized by Ralph N. Adams. Chemical analysis and detection of such events requires microsensors with rapid temporal responses since diffusion rapidly dilutes the local chemical changes. Carbon-fiber microelectrodes, with dimensions in the micron range, provide an ideal way to observe such chemical events in microdomains. Fluorescence microscopy also provides a convenient way to observe rapid chemical events in microdomains. The use of these tools to detect the chemical processes associated with neurotransmitter secretion from individual cells provides unique insight into the mechanisms involved in this process. These tools have been used at the level of single neurons as well as in intact tissue. Measurements with these tools reveal the transient nature of chemical neuronal communication. In addition, the factors that control this communication such as transport, metabolism, and storage have been revealed. As well as providing new information on chemical processes at neurons, the measurements demonstrate the factors that are important in chemical analysis in microdomains.

Dedicated to
Wilhelm Simon

Wilhelm Simon

born in Fahrwangen (Switzerland) in 1929

died in 1992

Simon graduated in chemistry at the Swiss Federal Institute of Technology (ETH), Zürich, in 1953 and received a Ph.D. degree from the Department of Organic Chemistry of the ETH in 1956. He continued to work at this institute, became "Privatdozent" (1961) and Assistant Professor (1965) for instrumental methods of analysis. He was promoted to "ausserordentlicher Professor" in 1967 and to full professor in 1970. Since 1985 he was Full Professor of Analytical Chemistry at ETH.

In the beginning Simon's research interests included acid base equilibria using glass electrodes, automation of elemental analysis of organic compounds, instrumentation in vapor pressure osmometry and pyrolysis mass spectrometry. But soon he started his very successful research and development in the field of ion-selective electrodes (ISE) where he pioneered new ligands for liquid membranes (the "ETH compounds") and many applications in biology and medicine. He designed chemical sensors and developed high resolution separation techniques. Simon had written and coauthored more than 400 publications and several books. Moreover, he was well known for his active work on many boards and committees and his very intensive travelling.

THE W. SIMON LECTURE
FROM ISE TOWARDS VISE

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The development beginning with Ion-Selective Electrodes (ISE) and leading to Voltammetric Ion-Selective Electrodes (VISE) is described. Starting point are the well characterized ISE's based on neutral ionophores. By this some theoretical approaches pioneered by W.Simon and his colleagues and coworkers at the ETH Zurich will be discussed together with recent ideas originating still from the same "scientific school" to explain a super-Nernstian behavior. Ideas based on the assumption of a thermodynamic equilibrium are compared to those assuming a steady state situation of the charge transfer at the interface under study. Both allow satisfactory explanations and predictions for, e.g., changing sensitivities, selectivities, Hulanicki effect, and varying life times. Of special theoretical interest are in this respect ISE membranes in which the Hofmeister series is not followed. Can the study of complex impedance planes be of some help toward a success in this respect? Can theory lead to a straightforward development strategy for a certain analyte ion by omitting lengthy empirical work?

Based on the work of J. Koryta on the Interface of Two Immiscible Electrolyte Solutions (ITIES) a new class of electroanalytical sensors, the VISE could be developed at the ICB. Despite certain advantages concerning the temperature effect, the detection sensitivity of higher charged ions, and current control via an exactly controlled area leading to pre-calibrated sensors the voltammetric curves obtained with those electrodes show a lower linear range. However, they are also of some theoretical value with respect to the electrochemical equilibrium discussion. The resulting cv diagrams allow the allocation of kinetically or diffusion limited currents and their superposition might lead to some new insight into the microscopic events at the phase boundary of interest. Modern screen printed techniques allow the construction of all solid-state VISE for single or multiple use. Considering the similarities of VISE with the metal/electrolyte interface first experiments indicate the possibility for enrichment steps by pre-electrolysis at a right potential followed by an electrochemical stripping process. This might open further exciting applications for many of the famous ionophores synthesized thus far by W. Simon and his group at the ETH.

Dedicated to
Veniamin G. Levich

V.G. Levich (Veniamin Grigorievich)

born in Charkov (Russia) in 1917

died in 1987

Levich studied physics and graduated at the University of Charkov in 1937. He worked at the Institute of Physical Chemistry at the USSR Academy of Sciences (1940-1958) and later at the Institute of Electrochemistry (headed by A.N. Frumkin) of this Academy in Moscow. Levich emigrated to Israel and spent his last years in the U.S.A.

Levich can be regarded as a pioneer for hydrodynamic electrochemistry. His fundamental contributions to theoretical physics and physical chemistry have only been worldwide detected after the publication of the English translation of his monograph "Physicochemical Hydrodynamics" in 1962 (first Russian edition published in 1952). Textbooks on electrochemistry refer to him in the field of rotating disk electrodes where the Levich equation describes the mass-transfer-limited condition for the current response.

THE V.G. LEVICH LECTURE

**ELECTROCHEMISTRY IN ULTRASMALL ENVIRONMENTS: CELLS,
NANOVIALS, AND MICROFABRICATED DEVICES**

Andrew G. Ewing

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We have developed ultrasmall electrodes for microscale and nanoscale chemical environments. Ultrasmall carbon fiber electrodes have been used to oxidize neurotransmitters released in single exocytosis events at individual cells. These events involve zeptomole levels of transmitter and vary with pharmacological manipulation. We have modeled the electrochemical response and can determine the total amount of transmitter released, the concentration of transmitter, and the size of the vesicle for each release event. To model the response of carbon fiber electrodes in ultrasmall environments, we have carried out voltammetry in picoliter nanovials made by lithographic impressions in polystyrene. Electrochemistry is nearly unique in its ability to be used in ultrasmall environments. This is clearly a large advantage when using electrochemistry for detection in liquid phase separations. Electrochemical detection has been used in electrophoresis with capillaries having diameters down to 450 nanometers and with channels as thin as 600 nanometers.

Dedicated to

Hans-Wolfgang Nürnberg

born in Köln, Germany, in 1930

died during a lecture trip to Canada in 1985

Nürnberg studied chemistry at the universities of Köln and Bonn, obtained a diploma degree in 1956, a Ph.D. degree from the University of Bonn in 1959 and the habilitation (D.Sc.) in 1968. He became scientific assistant at the Institute of Physical Chemistry, University of Bonn, in 1956, moved to the Max-Planck Institute for Iron Research for two years and joined the former Nuclear Research Centre Juelich (now "Research Centre Juelich") in 1962 as Head of the Central Laboratory for Chemical Analysis. In 1968 he was appointed Director of the Central Institute for Analytical Chemistry, later restructured and renamed as Institute of Applied Physical Chemistry. Since 1971 he was also Professor of Physical Chemistry at the University of Bonn.

Nürnberg was one of the pioneers for the development and application of polarographic methods for environmental studies. Based on his background in electroanalytical and physical chemistry he initiated and directed major studies of heavy metals in aquatic and terrestrial ecosystems including the characterization of wet deposition. His research interests included also bioelectrochemistry, especially the behavior of nucleotides at electrodes, and analytical methods for nuclear research. Nürnberg was one of the promoters for environmental specimen banking and was known for his active and global international cooperation. He has authored and coauthored a large number of publications and edited several books in the fields of analytical and environmental chemistry.

THE N.-W. NÜRNBERG LECTURE

VOLTAMMETRY IN AQUATIC SYSTEMS: PAST, PRESENT AND FUTURE
IN HONOUR OF PROFESSOR H-W. NURNBERGJ. Bufflé¹, M-L. Tercier-Waeber¹, M. Koudelka-Hep²¹ Department of Inorganic, Analytical Chemistry, University of Geneva, CH² Institute of Microtechnology, University of Neuchatel, CH

Professor H-W. Nurnberg has been a pioneer in developing the applications of voltammetric techniques in environmental systems. He early recognized that voltammetric techniques are amongst the very few enabling to perform routine analysis of Cu, Pb and Cd in sea waters, on board ship, despite their very low concentrations (10^{-10} to 10^{-8} M). He showed how to avoid contaminations from the ship itself, during sampling and sample handling. He was also strongly influenced by Heyrowsky concepts of polarography, and in cooperation with Dr. P. Valenta, he did much to develop voltammetric determination of metal speciation in waters, based on these concepts. H-W. Nurnberg realised that to understand and predict the environmental rôle and fate of metals (bioavailability, bioaccumulation, sedimentation), cheap and reproducible voltammetric instrumentation capable of performing in situ, real-time monitoring of specific metal species was required.

The design of such tools however became only possible with the development of microelectrodes. In particular, micron sized Hg semidrop deposited on Ir microelectrodes are stable and for at least 10 days without renewal. A major problem of in situ measurements in waters is the fouling of the electrode by natural organic matter and colloids. A novel sensor based on gel integrated Hg plated Ir based microelectrodes (GIME) has been developed to overcome this problem. The so-called dynamic metal species, i.e. those with diffusion and chemical dissociation fast enough to give rise to a reduction current are specifically measured. Note that those species are also the important ones to predict metal bioavailability. Because spherical diffusion occurs around a microelectrode, anodic stripping techniques can be used directly in the gel, and are not perturbed by the convection of the test natural medium. A complete submersible voltammetric instrument (the Voltammetric In Situ Profiler = VIP) has been developed to perform at depth measurements and speciation of metals with this reliable sensor.

The above sensor can be readily produced by thin-film microtechnology. The application of microtechnology to rugged integrated (electro)analytical systems is still in its infancy, but is very promising. Micropotentiostat can be produced on chips. Individually addressable electrode arrays enabling simultaneous voltammetric measurements up to 64 GIME, for high spatial resolution (200 μ m) at the sediment-water interface will also be described. Above all, applications of voltammetry can be considerably broadened to metal anions and organics, by combining a chemical or microbial microreaction chamber with voltammetric

or amperometric detection, as shown with the glass capillary based microsensors NO_3^- , H_2S , or CH_4 . The integrated combination of permeation liquid membrane to voltammetry based on microtechnology, is another original example of a microanalytical system including a species sensitive preconcentration device, for the in situ real-time analysis of metals or organics in the pico- to nanomolar range.

In general, non perturbing in situ, automatic, analytical systems will become more and more important in the future, for environmental monitoring. Thanks to its simple instrumentation, high sensitivity and intrinsic speciation capabilities, it can be expected that electroanalytical chemistry combined to microtechnical systems will play a very important rôle in this area, in the future.

ORAL CONTRIBUTIONS

IN-SITU MONITORING OF CONCENTRATION PROFILES BY CHRONOAMPEROMETRY USING AN ULTRAMICROELECTRODE PROBE

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All electrochemical techniques developed for the elucidation of reaction mechanisms rely on current or potential measurements and on their variations as a function of adjustable parameters like time scale and reagents concentrations. However even though the current is correlated to the concentration gradients taking place within the diffusion layer of an electrode, such purely electrical measurements cannot provide any direct information on the whole structure and composition of the diffusion layer.

Recently, we have demonstrated by chronoamperometry that concentration profiles generated at a larger electrode could be directly mapped with a probing ultramicroelectrode. Using this method the dynamic growth of a diffusion layer building-up at a planar electrode was monitored for a one reversible electron transfer. At short times ($t < 50$ ms) a perfect Cottrellian behaviour was indeed observed. At longer times, concentration profiles deviate from the Cottrellian prediction because of the progressive interference of natural convection, which prevents the expansion of the diffusion layer to infinite distances. The ensuing concentration profiles behave then almost as predicted within the classical Nernst layer approximation framework. A model of the convective mass transport based on a former Levich's approach accounts extremely well for the concentration variations observed experimentally by this method over all the time range investigated.

MANIPULATION AND CHARACTERIZATION OF MICROSCOPIC BIOCHEMICALLY ACTIVE REGIONS BY SCANNING ELECTROCHEMICAL MICROSCOPY

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Miniaturization of analytical systems has been a prevailing trend for the last decades. This trend includes electrochemical sensors and assays which have to meet new requirements set up by high-throughput testing and parallel processing. While the last years have seen considerable progress in DNA chip technology, an equally versatile technology for more delicate enzymes and antibodies is still missing. By sequentially using the scanning electrochemical microscope (SECM) for prototyping and characterization two issues vital to the progress in the field can be addressed:

- Which possibilities do exist to confine the immobilization of proteins dissolved in buffer to microscopic regions of a macroscopic surface?
- Are there designs to prevent cross-talk between neighboring sensitive regions by diffusing reactants?

One approach starts from surfaces passivated by self-assembled monolayers which are destroyed locally by SECM in the direct mode using AC current [1]. The activated areas are used to bind enzymes via terminal-functionalized thiols. Alternatively enzymes and antibodies were attached to microscopic magnetic beads which were assembled as agglomerates on surfaces [2] and showed promising results in miniaturized assays [3]

The rationale is discussed for selecting imaging condition in the feedback and generation-collection modes of the SECM for a given enzyme. Examples for reducing the cross-talk between sensitive regions include scavenger reactions in the solution bulk, and scavenging reaction taking place at the surface regions between the sensitive regions and have been followed by SECM.

References

- 1 T. Wilhelm, G. Wittstock; *Mikrochim. Acta* in press
- 2 C.A. Wijayawardhana, G.Wittstock, H.B. Halsall, W.R. Heineman; *Anal. Chem.* in press
- 3 C.A. Wijayawardhana, G.Wittstock, H.B. Halsall, W.R. Heineman; *Electroanalysis* in press

USE OF SECM AS A TOOL FOR AMPEROMETRIC DETECTION IN THIN-LAYER CHROMATOGRAPHY

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Thin layer chromatography (TLC) is a simple traditional analytical technique widely employed for the separation and identification of numerous organic and inorganic species in mixtures. Although, TLC is often employed for qualitative analysis, methodologies for quantitative detection of an analyte are also available in the literature. Quantitative detection is usually accomplished by elution of the analyte spot from TLC stationary phase. This requires a manually intensive procedure, which is often time consuming. Development of on-plate quantitation methods would therefore be desirable, to make the separation and detection processes indistinct from one another, in a manner similar to HPLC analysis. The majority of efforts in developing reliable on-plate detection schemes have been spectroscopic in nature. Recently a few investigations have also been concerned with direct on-plate quantification by voltammetry and amperometry.

Scanning Electrochemical Microscopy (SECM) is a technique that provides unique quantitative insights into reactions at solid/liquid interfaces. Actually, in the TLC process the analyte undergoes a series of adsorption/desorption stages from a silica stationary phase, which is equilibrated with a liquid mobile phase. Thus, SECM might be useful for the quantitative detection on the TLC plate provided the analyte is electroactive. The vast number of organic and inorganic species that are electroactive prompted us to explore the possibility to use a SECM apparatus as a voltammetric (or amperometric) detector in TLC analysis.

Explorative experiments have been carried out on simple electroactive molecule and synthetic solutions. In particular, we report on the electrochemistry of $K_4Fe(CN)_6$ and Ferrocene on silica TLC plates equilibrated with aqueous and acetonitrile solutions either without or with supporting electrolytes. Platinum and gold microelectrodes have been employed as electrode tips in the SECM experiments. Quantification of ferrocene in typical TLC development experiments, using on-plate calibration curves, has also been performed. Preliminary results have shown that sub nanomoles of the latter species can be detected.

DEVELOPMENT OF SELECTIVE ELECTRODES FOR HEAVY METALS USING SELF-ASSEMBLED MONOLAYERS AND THIN POLYMERIC FILMS

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Self-assembled monolayers offer significant advantages in electroanalytical chemistry. We have been involved in the application of functionalized self-assembled monolayers as a means of designing highly sensitive and selective electrodes for heavy metals (1-2). We wish to present our results in which we focus not only in the application of these monolayers for selectively extracting metal ions but also on their structural analysis.

Two systems will be presented. We will demonstrate different approaches for structuring an interface that is selective toward iron ions. This has involved the application of both thin polymeric films and self-assembled monolayers consisting of a sulfonate functionality. Two major approaches have been examined, namely, the formation of a specific complex in the solution followed by its selective extraction and the selective extraction of iron(II) or iron(III) by a structured interface.

The second system focuses on a 6-mercaptohexanoic acid monolayer assembled on Au and studied by the scanning electrochemical microscope (SECM). The essence of this study has been to develop methods for determining the heterogeneous complexation constants of metal ions by functionalized monolayers. As a model system we have examined the association of cadmium(II) by carboxylate end groups. The feedback current measured at a Pt microelectrode upon oxidation of IrCl_6^{3-} , while approaching a carboxylate terminated-monolayer, is affected by the charge of the layer. The addition of Cd^{2+} or protons changes the feedback from negative to positive and allows determining the pK_a and the association constant of Cd^{2+} by the monolayer.

References

1. a.) D. Mandler, I. Turyan, *Electroanal.* 1996, 8, 207. b.) *ibid*, *Anal. Chem.* 1994, 66, 58.
c.) *ibid*, *Anal. Chem.*, 1997, 69, 894.
2. I Turyan, D. Mandler, *Isr. J. Chem.* 1997, 37, 225.

ELECTROANALYSIS IN DYNAMIC MICROSYSTEMS WITH HIGH LOCAL RESOLUTION

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Microsystem technologies require a high precision of processes and a homogeneity of products in the μm scale. On the other hand, the processes take place in microstructures with high aspect ratios. Hence, it is a challenge for electrochemists to control the processes in the μm scale with high local resolution.

Ion-selective electrodes are available for some years. The problem consists in the miniaturization. Using various technologies for conducting and insulating materials, microelectrodes now are available with a radius down to 100 nm and an aspect ratio up to 100. Potentiometric and amperometric electrodes were developed.

As a first example, the potentiometric pH analysis is described for the phosphating process of steel. During this process, an inhomogeneous crystallite layer of some μm thickness is formed within 100 sec. This process is controlled by the local pH shift caused by cathodic hydrogen evolution or accelerator reduction. At first, concentration gradients of protons were measured in model systems during cathodic hydrogen evolution on platinum. In a second stage, the phosphating process itself was controlled. pH shifts of 1 to 3 units were measured. Measurements with the local resolution of 1 μm yielded a diffusion layer thickness of about 10 microns. The influence of the accelerator and additions of nickel ions are evaluated. The consequences for the formation of the local element are derived.

Another example refers to the control of the metal concentration profile in microstructures during the LiGA process. For this purpose, amperometric electrodes were applied which allow the simultaneous determination of 2 cations. Examples are described for the deposition of Cu/Ni alloys. Measurements were successful up to an aspect ratio of 4.

ELECTROANALYSIS WITH SILICA-MODIFIED ELECTRODES

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Notwithstanding the attractive surface properties of pure silica, the numerous forms of organically-modified silicates obtained by grafting organic groups to the silica backbone, and the versatility of sol-gel chemistry to prepare a wide range of materials with tailor-made characteristics and properties, the implication of silica-based solids in electrochemistry is rather recent. Indeed, these materials display fascinating surface chemistry (i.e. adsorption capacity, acid/base chemistry, ability to be chemically modified) and they can be prepared with selected chemical and physical characteristics that could be advantageously exploited in electroanalytical chemistry. The purpose of this communication is to give a short overview on the electroanalytical applications of silica-modified electrodes including the preparation methods, their basic electrochemical characterization, and their interest in chemical sensing or in the development of biosensors [1]. Special emphasis will be laid on electrodes modified with pure silica (amorphous or crystalline) which were particularly studied in our group [2, 3].

Three main strategies were applied to fabricate silica-modified electrodes: (1) the dispersion of a silica-based solids within a conductive composite matrix (mainly carbon paste), (2) the deposition of a silicate or an organically-modified silicate on a solid electrode surface, and (3) the preparation of ceramic-carbon composites. Examples of analytical applications include the preconcentration of analytes prior to their electrochemical detection, ion exchange and permselectivity at the electrode surface, or the field of biosensors by exploiting the efficient immobilization of the enzyme and/or the mediator in sol-gel silicates. In particular, the presentation will focus on the use of pure silica as an electrode modifier for the accumulation of heavy metal species as Cu^{II} and Hg^{II} . The interest of the recently discovered crystalline mesoporous silicas will be discussed.

References

- [1] A. Walcarius, *Electroanalysis*, **10** (1998), 1217.
- [2] A. Walcarius, J. Bessière, *Chem. Mater.*, **11** (1999), 3009.
- [3] A. Walcarius, J. Devoy, J. Bessière, *Environ. Sci. Technol.*, **33** (1999), 4278.

CARBON FILM ELECTRODES AND APPLICATION IN ELECTROANALYSIS

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In the constant search for new electrode materials there has recently been particular interest in new solid electrode materials to substitute mercury in the negative potential range, owing to concerns with regard to its environmental toxicity. For example, in stripping voltammetry it is often necessary to reach potentials of -1.5 V vs. SCE. The hydrogen overpotential of liquid mercury or of mercury thin film electrodes is sufficient for this purpose. Efforts to procure substitutes have included boron-doped diamond and nitrogen-incorporated tetrahedral amorphous carbon.

In this work, electrodes were made from carbon film resistors of 1 ohm and 5 ohm resistance. Their voltammetric properties have been studied and compared with those of commercially available glassy carbons, before and after electrochemical pre-conditioning. The potential window has been measured in different aqueous solutions and the behaviour of common electroactive species such as ferrocyanide examined. Promising results have been obtained for the anodic stripping voltammetry of a number of metal ions, particularly zinc ion.

ACKNOWLEDGEMENT

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BIOSENSORS BASED ON MEMBRANE-BOUND ENZYMES IMMOBILIZED IN A MEMBRANE MIMETIC LAYER ON GOLD ELECTRODES

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Amperometric biosensors based on membrane-bound enzymes, in particular D-Fructose Dehydrogenase (FDH), D-Gluconate Dehydrogenase (GADH) and L-Lactic dehydrogenase (cytochrome b₂) (Cyb₂), immobilized in a membrane mimetic layer on a gold electrode has been constructed and tested. A bare gold electrode first was modified through chemisorption of 5-(octyldithio)-2-nitrobenzoic acid (ODTNB). The membrane bound enzyme was deposited simply by adsorption. ODTNB include a long-chain in a short-length thioacid, providing an heterogeneous like alkanethiol layer after adsorption on gold electrodes. The short-length thioacid may provide electrostatic interactions with enzyme surface charges, while the alkanethiolate enable hydrophobic interaction with the largely lipophilic, membrane-bound enzymes. The binding reaction of the enzyme (FDH, GADH, and Cyb₂) with ODTNB-modified gold surfaces has been studied with the quartz crystal microbalance. Spectrophotometric and electrochemical assays indicate that the immobilized enzyme retains its enzymatic activity after immobilization onto the ODTNB modified gold surface. The amount of immobilized (and active) FDH, GADH and Cyb₂ was estimated from QCM to be of the order of 2.5×10^{-12} , 5.3×10^{-12} and 3.7×10^{-12} mol. cm⁻², respectively. A fructose and a gluconate biosensor were developed making use of a gold electrode modified with ODTNB and FDH or GADH, respectively. Ferrocenemethanol was employed as mediator in solution. The calibration curves exhibited a linear relation between the biosensor response and the substrate concentration (fructose or gluconate) over the range 0.1 - 0.6 mM. Statistical analysis gave an excellent linear correlation ($r = 0.997$) and a sensitivity of 2.59 mM⁻¹ for fructose. The biosensor is stable, when it is stored at 4°C, for at least 25 days in spite of repeated rinsing and cyclic voltammetry studies run to steady state. The membrane mimetic layer effectively blocked access of interfering substances, such as ascorbic acid.

ELECTROCHEMICAL DETECTION OF LARGE SINGLE PARTICLES

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Current-time curves of a single redox particle might display images of an electrode reaction pathway. However, they include large noise. The large noise can be overcome if the number of electron transferred, n is large in a particle. Making a large redox particle may be realized by use of conducting polymer-coated microspheres, of which candidate is a polyaniline-coated polystyrene latex (PAPS). We synthesize the PAPS and obtained pulse-like current in chronoamperometry.

The polystyrene latex was polymerized with styrene and polypyrrolidone (surfactant) in 2-propanol. It was coated with polyaniline by chemical polymerization of aniline to yield PAPS. The PAPS was suspended in an acidic solution. It was mostly monodispersed, 1.5 μm in diameter, detected with an optical microscope.

The voltammogram at a microelectrode showed an anodic wave under the steady-state, which was 0.2 V shifted from the CV of the film cast the PAPS. A value of n was determined by bulk electrolysis, and is 1.2×10^8 . The steady-state currents included many noises. The Fourier transformed currents are, however, show peaks at 14 Hz for a low concentration and ca. 25 Hz at a high concentration (Fig.1). No band was observed for the blank solution (1.2 M HCl) and the $\text{Fe}(\text{CN})_6^{4-}$ solution. The inversely transformed current after eliminating 60 Hz shows periodical waves with 70 ms peak-to-peak width. The periodicity is ascribed to the oxidation of the single particle.

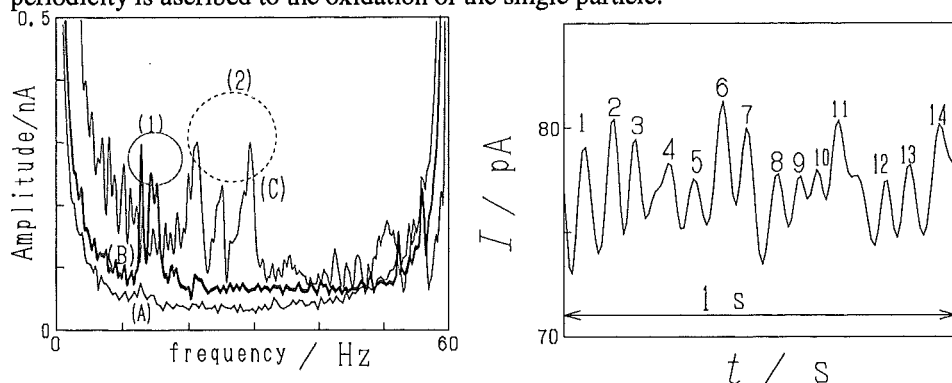


Fig.1. Spectra of the Fourier transformed currents of (A) 1.2 M HCl solution, (B) PAPS+1.2 M HCl with the steady-state current 0.125 nA, (C) PAPS+1.2 M HCl with the steady-state current 0.24 nA.

Fig.2. Inverse Fourier transformed current for (B), in which real and imaginary components at frequencies more than 40 Hz were eliminated and then were inversely transformed.

ELECTROANALYSIS IN THE EXTRACELLULAR SPACE OF THE BRAIN WITH ENZYME-MODIFIED CARBON FIBER MICROELECTRODES

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Monitoring of glutamate, choline, and glucose in brain tissue with amperometric sensors based on carbon fiber microcylinder electrodes modified with a crosslinked redox-polymer gel containing entrapped enzymes will be described. Glutamate is of interest because it is an excitatory neurotransmitter in many neuronal pathways. Choline is of interest because it is a potential marker for acetylcholine. Glucose measurements provide a useful control.

Carbon fiber microelectrodes (7 μm diameter, 300-400 μm long) are modified with redox polymer, crosslinking agent, horseradish peroxidase, ascorbate oxidase, and one of the following: glutamate oxidase, choline oxidase, or glucose oxidase. The sensors are cured at 37°C in air for 1 hr and then coated with Nafion [1, 2]. The sensors, which are operated at -100 mV vs Ag/AgCl, are confirmed to respond to analyte without interference from physiologically relevant concentrations of ascorbate (400 μM).

For *in vivo* work, a microsensor and a microinfusion pipet are implanted side by side in the brain of an anesthetized rat. Infused solutions (~100 nL) contain either the analyte, the enzyme that destroys the analyte, or a drug. In all cases, the signals increase during infusion of analyte and decrease during infusion of the destructive enzyme. Glutamate and choline signals decrease during infusion of tetrodotoxin (which blocks spontaneous neuronal activity), glutamate signals increase during infusion of PDC (a glutamate uptake inhibitor), and choline signals decrease during infusion of neostigmine (a cholinesterase inhibitor). These drugs do not affect glucose signals.

These results provide evidence that the amperometric signals observed *in vivo* are related to the neurochemical activity of the brain. These sensors appear to have considerable potential as tools for neurochemical research.

References

1. Shankar L., Garguilo M.G., and Michael, A.C. (1998) Enzyme biosensors based on redox polymers. In *Methods in Biotechnology*, Vol 6, Mulchandani A. and Rogers K.R. eds. pp 121-132. Humana Press, Totowa, NJ.
2. Kulagina N.V., Shankar, L., and Michael A.C. (1999) Monitoring glutamate and ascorbate in the extracellular space of brain tissue with electrochemical microsensors. *Anal. Chem.* **71**, 5093-5100.

DIRECT ELECTRON TRANSFER OBSERVED FOR PEROXIDASE TO SCREEN-PRINTED GRAPHITE ELECTRODES

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Horseradish Peroxidase (HRP) is one of the often used enzymes in biochemical analysis due to its high specificity for hydrogen peroxide and its high specific activity. Thus, it is used in combination with oxidases and as label in enzyme immunoassays. A number of these applications are based on photometric detection as the co-substrate for hydrogen peroxide can be a dye changing colour due to the enzyme reaction. However, with respect to the development of enzyme electrodes for substrates of oxidases also electrochemical transduction principles are attractive. They can be utilized either by using co-substrates which are electrochemically active, such as hydroquinone which is oxidized by the enzyme to benzoquinone, or by direct electrochemical regeneration of the peroxidase requiring the transfer of electron from the electrode directly to the enzyme. Up to now, this direct electron transfer was observed mainly using graphite or carbon paste electrodes onto which HRP was adsorbed. As screen-printed electrodes find increasing application as they can easily be produced under industrial conditions we examined the possibilities to use this type of electrodes for the detection of HRP-enzyme activity. For the production of screen-printed graphite electrodes different pastes can be used leading to electrodes of different electrical conductivity and electron transfer rates to the mediator couple benzoquinone / hydroquinone. Exchange currents between mediator and electrodes were determined, and proved to be approx. 10% of those achieved for a conventional glassy carbon electrode for the best screen-printed electrodes. One of these optimal electrodes was tested for direct electron transfer to HRP. Maximum currents in the range of up to 100 nA were found when high concentrations of HRP were adsorbed on the screen-printed graphite electrode surface and the resulting enzyme layer was covered by a membrane polymerized by UV-light. The electrodes responded to hydrogen peroxide concentrations from approx. 10 μM to up to 1 mM. From the known 3-dimensional structure of the enzyme its orientation to the electrode surface was modelled showing separation of the protein from the electrode surface by carbohydrate residues. Thus, it is expected that electron transfer rates increase with the use of a not-glycosylated enzyme, i.e. a recombinant enzyme. Results achieved with the different enzyme preparations will be presented.

CONTROLLED ELECTROCHEMICAL RELEASE OF DNA AND DNA/LIPID COMPLEXES

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This presentation will report on a new non-viral route for delivering DNA based on an electrochemically-triggered release. The basic concept is to immobilize the nucleic acid or the DNA/lipid complex onto an electrode surface and to release it, as needed, under potential control. The ability to electrically modulate the interfacial properties, coupled to the miniaturization, safety, and low-cost advantages of electrochemical systems, make them extremely attractive for delivering the genetic material. Conducting-polymer modified electrodes were used earlier for an electrical release of neurotransmitters. However, the large size of DNA dopants precludes their undoping from such films. In contrast, electrochemically-induced release of nucleic acids from gold and carbon microelectrode surfaces can be readily accomplished in connection to electrostatic repulsion or reductive cleavage of adsorbed or self-assembled DNA layers, respectively. Various tools, including quartz crystal microbalance, XPS or voltammetric blocking experiments have been employed for characterizing the on-demand removal of the nucleic acid from the surface. The new electrically-driven protocol represents a potentially attractive non-viral alternative for releasing the genetic material to specific locations at selected times, in a safe and cost-effective manner.

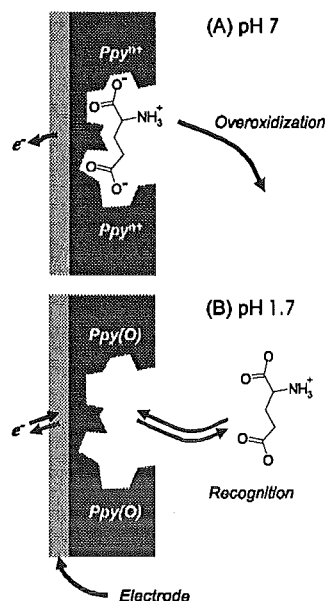
POTENTIAL-INDUCED ENANTIOSELECTIVE UPTAKE OF AMINO ACID INTO MOLECULARLY-IMPRINTED OVEROXIDIZED POLYPYRROLE

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Conducting polymers have attracted much attention for a number of applications, such as batteries, sensors, ion-selective membranes and electronic devices. Polymers such as polypyrrole and polyaniline incorporate anionic dopant to compensate for the cationic charge carried by their backbones. It has been reported that dopant determines the porosity of the polymer (network spacing) and this feature has been utilized for ion selective electrodes to recognize some inorganic anions selectively. However, it has not been made clear yet, if conducting polymers can detect molecular details in a more precise manner through the cavity created by dopant, based on the molecular imprinting protocols. We report here that such recognition becomes possible, if polypyrrole film is dedoped by overoxidation.

The PPy/L-glutamate films used here were deposited galvanostatically on Pt-coated AT-cut quartz crystals in an aqueous solution containing 0.5 M pyrrole and 1.0 M sodium L-glutamate (glu). These films were then overoxidized potentiodynamically in a range of -0.3 to 1.0 V in a pH 6.9 phosphate buffer (Fig. A). A negatively charged overoxidized film took up $\sim 60 \text{ nmol cm}^{-2}$ L-glu and $\sim 6 \text{ nmol cm}^{-2}$ D-glu (Fig B). The EQCM and voltammetric behavior of the overoxidized PPy/D-glu film was exactly opposite to that for the PPy/L-glu film. However, without overoxidation, the voltammetric and frequency-potential curves failed to reveal any significant differences between both the isomers. This highlights the importance of the overoxidation treatment in our procedures, which hardens the polypyrrole texture to allow the templated cavity to memorize the molecular details after dedoping.



ALL-SOLID-STATE Ag^+ -ISE BASED ON [2,2,2]P,P,P-CYCLOPHANE

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All-solid-state ion-selective electrodes (ISEs) based on two ionophores with similar structure, *i.e.* [2,2,2]p,p,p-cyclophane and [2,2,2]m,p,p-cyclophane were prepared and investigated. The ion-selective membranes were composed of the corresponding ionophore (1 %), potassium tetrakis(4-chlorophenyl)borate (0.5 %), 2-nitrophenyl octyl ether (65 %), and PVC (33 %). The ion-selective membrane was placed on top of a layer of the conducting polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), which was electrochemically deposited on glassy carbon. The PEDOT film was conditioning in 0.01 M AgNO_3 for and then coated with the ion-selective membrane by solution casting. The PEDOT film is an ion-to-electron transducer (solid contact) between the ionic conducting ion-selective membrane and the electronic conducting glassy carbon substrate [1,2]. The resulting all-solid-state ISEs were conditioned in 0.01 M AgNO_3 and investigated as Ag^+ -ISEs, because [2,2,2]p,p,p-cyclophane is known to be selective to Ag^+ [3].

The results show that [2,2,2]p,p,p-cyclophane is selective to Ag^+ , whereas [2,2,2]m,p,p-cyclophane is not. In the case of [2,2,2]p,p,p-cyclophane, $\log K_{\text{Ag},j} \approx -4 \dots -7$, for the following ions: Zn^{2+} , Pb^{2+} , Ca^{2+} , Fe^{3+} , Mg^{2+} , Cu^{2+} , Co^{2+} , Al^{3+} , NH_4^+ , Cd^{2+} , Ni^{2+} , H^+ , Li^+ , Na^+ , K^+ determined by the separate solution method. Among the inorganic cations tested, the strongest interference was observed for Hg^{2+} ($\log K_{\text{Ag},\text{Hg}} \approx -1$).

The closely related ionophore, [2,2,2]m,p,p-cyclophane, showed rather poor selectivities for Ag^+ , *i.e.* $\log K_{\text{Ag},j} \approx -2 \dots +1.5$, for the cations mentioned above, *e.g.* $\log K_{\text{Ag},\text{Hg}} \approx 0$. The ionophore [2,2,2]m,p,p-cyclophane, however, showed a relatively high selectivity for pyridinium (Py^+) ($\log K_{\text{Ag},\text{Py}} \approx +1.5$) in comparison with [2,2,2]p,p,p-cyclophane ($\log K_{\text{Ag},\text{Py}} \approx -1.5$).

Reference

1. A.Cadogan, Z.Gao, A.Lewenstam, A.Ivaska and D.Diamond, *Anal. Chem.*, 64 (1992) 2496
2. J.Bobacka, *Anal. Chem.*, 71 (1999) 4932
3. J.Gross, G.Harder, A.Siepen, J.Harren, F.Vögtle, H.Stephan, K.Gloe, B.Ahlers, K.Camman and K.Rissanen, *Chem. Eur. J.*, 2 (1996) 1585

LATERAL DEPOSITION OF ENZYME-CONTAINING POLYMERS AS A BASIS FOR MINIATURISED AMPEROMETRIC BIOSENSORS

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Miniaturisation of biosensors is important for their possible future application especially for continuous monitoring in medical analysis. Obviously, in order to guarantee high spatial resolution and good reproducibility non-manual deposition of the sensor compounds on top of the transducer surface is indispensable. In this respect, the electrochemical-induced formation of sensing layers exclusively on the surface of (micro)electrodes has found increasing interest in the past years [1].

Here, we want to report on two different approaches using electrochemical formation of polymer layers with integrated biological recognition elements. The described film formation processes allow us in principal to vary the sensor architecture, to integrate redox-relays to ensure fast electron-transfer rates between the active site of the enzymes and the electrode surface, and to add additional polymer layers in order to reduce the influence of interfering compounds.

In the first approach, a non-conducting polymer film is deposited on a micro-electrode surface controlling its lateral structure by means of scanning electrochemical microscopy (SECM). Using a potentiostatic pulse-deposition regime, the polymer film can be obtained in less than one second integrating the biological recognition element in general with high activity. The polymer film can be chemically modified by introducing redox relays, charged side-chains, and additional polymer layers with defined size-exclusion properties. Results concerning the formation of such micro-structured biosensors will be presented.

The second approach is based on the deposition of (two- and three-dimensional) polypyrrole structures with integrated enzymes using SECM. The deposition site and the dimensions of the obtained structures can be controlled by means of the dimensions of the used micro electrode. In addition, using pyrrole derivatives which are modified with Os-complexes or hydrophilic side-chains, the electron-transfer properties of the obtained polymer structures can be tailored. First results concerning the formation of polypyrrole micro-towers with integrated enzymes will be presented.

Reference

- [1] a) P. N. Bartlett, P. R. Birkin, *Synth. Met.* **61** (1993) 15-21 b) W. Schuhmann, *Mikrochim. Acta.* **121** (1995) 1-29. c) M. Trojanowicz, T. Krawczynski vel Krawczyk, *Mikrochim. Acta* **121** (1995) 167-181. d) S. Cosnier, *Biosens. Bioelectron.* **14** (1999) 443-456

COMBINING ELECTROCHEMISTRY AND SPECTROSCOPY INTO A SINGLE SENSOR

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The spectroelectrochemical sensor embodies two modes of instrumental selectivity (electrochemical and spectroscopic) in addition to selective partitioning into a chemically-selective film. The sensor consists of a planar optical substrate/electrode coated with the selective film. Sensing of analyte that partitions into the film is based on the change in the attenuation of light passing through the guided wave substrate that accompanies an electrochemical reaction of the analyte induced by electromodulation. Threefold selectivity for a chosen analyte is obtained by the choice of coating material, the electromodulation potentials, and the wavelength for optical monitoring.

The sensor concept has been demonstrated with an indium tin oxide coated glass guided wave device that has been over-coated with the following charge-selective thin films: sol-gel derived PDMDAAC-SiO₂ composite (where PDMDAAC = poly(dimethyl diallylammonium chloride), sol-gel derived Nafion-SiO₂ composite, and poly(vinyl alcohol)-polyelectrolyte blend. Model analytes that have been used to demonstrate the concept of this sensor are Fe(CN)₆⁴⁻, Ru(CN)₆⁴⁻, Ru(bipy)₃²⁺, Re(DMPE)₃¹⁺ (where DMPE = 1,2-bis(dimethylphosphino)ethane), and MV²⁺ (methyl viologen dication). Performance characteristics of the sensor such as selectivity, sensitivity, detection limit, response range, response time, and reversibility have been measured. Improvements in detection limit can be realized by ensemble averaging a repetitive signal modulated by a potential step or potential scan excitation signal. A small portable sensor unit including a virtual interface, control electronics and optics is being developed. Practical application of the sensor has been demonstrated with the determination of ferrocyanide in Hanford waste tank simulant solution.

ELECTROCHEMICAL DETECTION BY LUMINESCENCE FOLLOWING ELECTRON TRANSFER

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The problem with electrochemical detection is the electrode. It fouls, it needs polishing, it is temperamental. Certainly there are possibilities for using the chemistry of the electrode for selective detection, but for outer sphere and other rapid redox events, the electrode's surface chemistry is not so critical. We have looked with envy at the dramatic advances being made in detection limits in the laser-induced fluorescence community, and wondered if we could not achieve similar detection limits for electrochemical detection as others have in fluorescence. Thus, we have tried to find and employ molecules whose luminescence depends upon the redox state of the molecule. Through such molecules, we ought to be able to convert redox activity into fluorescence.

This was first achieved by us using $\text{Ru}(\text{bpy})_3^{3+}$ as a pre-luminescent reagent with solutes that were oxidizable, tyrosine- and tryptophan-containing peptides (Anal. Chem., 1999, 71, 1504). One useful aspect of this procedure is the almost complete absence of a baseline disturbance during a gradient elution separation. Within the limited set of peptides that we used (dynorphins) the number of electrons transferred was 1 for tyrosine and 4 for tryptophan. These numbers are different than those we obtained at electrodes, signifying differences in timescale and mechanism.

Recently, we have begun to attempt to apply this to more complex systems, explosives and Cu-peptide complexes. Each of these two classes of analytes has been determined by dual electrode electrochemical detection. Our work has been to replace the second, "collector" electrode with a prefluorescent reagent to improve detection limits. For the nitroaromatic and nitramine explosives, we reduce them at a carbon foam electrode, and then expose that stream to $\text{Ru}(\text{bpy})_3^{3+}$, while for the peptides, we oxide Cu(II) to Cu(III) and reduce the Cu(III) with dihydrodichlorofluorescein.

PULSED LASER DEPOSITION – AN INNOVATIVE TECHNIQUE FOR PREPARING INORGANIC THIN FILM SENSORS

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Within the last few years, silicon-based microsensors became more and more interesting for analytical purposes. One reason therefore is that their manufacturing is often fully compatible to semiconductor processing, resulting in miniaturizable and rugged sensor devices. However, the application of the sensitive layers, e.g. inorganic materials requires specific deposition techniques, since the different chemical and physical properties of the respective components, the total composition and the stoichiometry can be significantly disrupted during the deposition process.

To avoid this drawback, we suggest the employment of the pulsed laser deposition technique (PLD) as an innovative thin film preparation method for chemical sensors. For this process, a short ultraviolet laser pulse of high light intensity is used in order to vaporize material from a target and deposit thin film layers onto a substrate in a vacuum chamber. In contrast to conventional thin film techniques, the PLD process takes place independent on the composition of the target and due to its short process time, the well-defined and stoichiometric deposition is also possible in different gas atmospheres. Depending on the broad spectrum of wavelengths as well as on the pulse energy, this process can be used to deposit a large variety of compounds.

In this paper we describe the application of the PLD process for the realization of pH-sensitive layers on the basis of Al_2O_3 as well as chalcogenide-based layers that are suitable for the heavy metal detection. The pH sensors consisting of $\text{Al/p-Si/SiO}_2/\text{Al}_2\text{O}_3$ EIS (electrolyte-insulator-semiconductor) heterostructures, are highly stable in the long term and possess a nearly-Nernstian pH sensitivity of about 56 mV/pH. The chalcogenide glass layers have been deposited onto p-Si/Cr/Au substrates. Depending on the glass materials used, these potentiometric sensors show a high sensitivity towards Pb and Cu of about 25 mV/pPb and about 29 mV/pCu.

A SINGLE-STEP IMMUNOSENSOR BASED ON ELECTROCHEMICAL FLOW-INJECTION ANALYSIS FOR THE REAL-TIME MONITORING OF BIOSPECIFIC INTERACTIONS: APPLICATIONS IN ENVIRONMENTAL ANALYSIS.

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The basis of this work is the development of a simple, robust, single-step immunosensor that is capable of the *in situ* real-time monitoring of environmental pollutants. The herbicide atrazine was chosen as a model analyte. Our biosensor is based on an electrochemical screen-printed carbon paste electrode incorporating the electroactive polymer polyaniline. The system manipulates the thick film based technology of screen printing which is a viable and increasingly popular solution to the mass-production of cheap, low cost, disposable sensor devices. The system has also been integrated into a flow injection set-up.

Use of the conducting polymer polyaniline removes the need for diffusional electron transfer mediators in the sensor set-up. This establishes a novel electrically-wired immunosensor based on the concept that only redox reactions coupled to the electrode surface will result in significant changes in catalytic current. Ultimately this removes the need for a physical separation step in the assay, a factor which complicates existing heterogeneous immunoassay techniques and prohibits the realisation of real-time investigations. This is achieved without increasing the complexity of the assay.

The basis of this work is an investigation into the kinetic properties of antibody-antigen interactions, comparing and contrasting bivalent whole antibodies and monovalent Fab fragments to atrazine. It also compares the abilities of this electrochemical system to compete with established optical technologies such as BIAcore™. Ultimately, these results hope to establish a separation-free immunoanalytical technique, which allows for the realisation of the single-step, real-time, in-field monitoring of atrazine and other pesticides in a highly selective and sensitive fashion demanded by current EU legislation.

EXPLOITATION OF NON-AQUEOUS ELECTROCHEMISTRY FOR SEPARATION SCIENCE

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Electrochemists have utilized the attractive features of non-aqueous electrochemical systems for many years. The use of organic solvent systems in place of aqueous solutions can considerably widen the scope of electrochemical investigations. Important criteria for the choice of solvent and electrolyte are the accessible potential range, chemical inertness, solvent power and stability of electrochemical responses in the respective media. Acetonitrile is probably the most widely used solvent for non-aqueous electrochemistry as it offers excellent characteristics concerning the above criteria. Non-aqueous capillary electrophoresis (NACE) which is gaining increasing importance, particularly for pharmaceutical analysis, appears to be an ideal field for the application of electrochemical detection methods. In this contribution it is intended to demonstrate that acetonitrile-based NACE coupled with electrochemical detection (ED) can be exploited in various ways:

- i.) The well-defined voltammetric behaviour of ferrocene compounds in acetonitrile solutions can be utilized to perform fundamental studies regarding the methodology of NACE-ED. Effects of the high-voltage electrical field on detection performance and the mass transport situation in the vicinity of the capillary outlet can be characterized with spatial resolution. The results obtained are important for the optimization of end-column ED for NACE.
- ii.) The extended accessible potential range in acetonitrile solutions allows to detect compounds that are hardly oxidized. Practical applications for the analysis of alkaloids and water insoluble dyes will be shown.
- iii.) An important aspect for practical use is the enhanced reliability of electrochemical measurements in acetonitrile-based media. This will be demonstrated considering long-term stability of the detector response and the attainable precision of NACE-ED measurements.

**SOLID PHASE MICROEXTRACTION OF ANIONS OF ENVIRONMENTAL
INTEREST: APPLICATIONS OF CONDUCTING POLYMER MICROFIBER
ELECTRODES FOR INJECTION SYSTEM FOR HPLC AND EIA**

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Solid Phase Microextraction (SPME) using silica and bonded phase fiber membranes has been the subject of investigation by a number of groups for preconcentration of anionic analytes for analysis by ICP-MS or HPLC/ICP-MS. Although they have proven useful in some circumstances, they suffer from three major disadvantages – namely the necessity for derivatization of the surface to accomplish adsorption, the length of time required for the preconcentration and release steps of the analysis, and possibilities of fouling by matrix components.

At present, we are investigating the possibility of using poly-3-methylthiophene microfiber electrodes for uptake of anions of chromium, arsenic, etc. from aqueous solution. Our efforts have focussed on these anions due to the importance of developing sensitive assays for the various species present in environmental samples. After fabrication of the conducting polymer on a platinum microfiber substrate by cycling in a nonaqueous solution of the monomer, the polymer is immersed in the sample solution and converted to its positively charged form by application of a potential of an oxidizing potential. The arsenate then migrates into the polymer to preserve electroneutrality. Upon reversal of the potential to negative values, the polymer is converted back to its neutral hydrophobic form and the ions are expelled. The concentration procedure normally requires less than 3 min and desorption is complete in less than 2 sec. The typical time requirements are an hour or more for the conventional microfiber extraction. The choice of the polymer for each anion is very important as these species are electroactive. The redox potentials (and electron transfer kinetics) of the polymer must be chosen so that the valence states of these species in the environment does not change on uptake and release. Detection of picogram quantities of these anions are routinely possible and optimization of polymer formation, extraction and desorption potentials and times promise even lower detection limits. In addition, such polymer electrodes have been shown in prior studies not to be subject to fouling even in solutions containing high concentrations of proteins or surfactants. The electrode system has been designed to permit direct injection into HPLC and FIA instruments.

IN-ELECTRODE COULOMETRIC TITRATIONS: DETERMINATION OF NON-METALS

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Coulometry has become a routine tool for the most accurate determination of numerous electrochemically active species mainly at higher concentration levels. In flow-through stripping arrangements it is also suitable for the determination of lower even trace and ultratrace concentrations of some metals such as As, Hg, Cd, Pb, Se, etc., and some non-metals such as halogenides, sulphides. The main problem in trace analysis by coulometry, namely the accurate compensation of the relatively high underground signals can be solved by making use of porous electrodes facilitating high recoveries and providing low background signals combined with the deposition/stripping approach.

The unique structure of porous electrodes resulting in thin-layer cell properties facilitates simple galvanostatic coulometric titrations where the porous electrode acts both as the generating and the indicator electrode. Here, the sample inside the electrode is titrated by constant current whereas the potential of the electrode is monitored and evaluated. Owing to the thin-layer properties of the porous electrode material, the oxidation-reduction reactions are virtually limited by the electrode reaction only.

Higher analyte concentrations can easily be determined by making use of this in-electrode coulometric titration (IECT) concept: The porous electrode is filled with the sample solution and the analyte species are electrochemically titrated in the electrode bulk. By knowing the effective volume of the pores, the analyte contents can easily be calculated by making use of the Faraday's laws. The main applications of IECT are as follows:

- I. Acid-base titrations (determination of HCl, NaOH, etc),
- II. Precipitation titrations (determination of Cl^- , Br^- , I^- , etc.),
- III. Oxidation-reduction titrations (determination of Fe, Cr(VI), NH_3 , PO_4^{3-} , etc.) and
- IV. Complexometric titrations (e.g. evaluation of the complexing capacity of waters).

Dissolved oxygen may interfere in some titrations, e.g. during the determination of acids. This can be solved by inserting a flow-through oxygen scavenger to the flow.

The main advantages of IECT are simplicity, speed and acceptable accuracy and precision.

**RECENT ADVANCES IN CATALYTIC CATHODIC STRIPPING
VOLTAMMETRY: SELENIUM, AND THE CHEMICAL SPECIATION OF
COBALT**

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The sensitivity of electroanalytical methods is pushed to its limits by very low levels of trace elements in uncontaminated natural waters. Our work has shown that the sensitivity of cathodic stripping voltammetry (CSV) is much enhanced using catalysis. Using a catalytic method for cobalt we have determined the chemical speciation of cobalt in seawater, at levels of 50 pM cobalt: it was found that cobalt is strongly complexed by natural organic ligands, leaving the free, uncomplexed, cobalt at femtomolar levels. We also developed a new method for selenium based on its catalytic effect on the generation of hydrogen. It will be demonstrated that using this method selenium can be detected at pM levels in natural waters. These catalysed methods firmly place CSV amongst the most sensitive analytical methods for elements in natural waters.

AC VOLTAMMETRY WITH APPLIED ALTERNATING POTENTIAL OF ANY AMPLITUDE

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Ac voltammetry [1, 2] has many merits as an electroanalytical technique, but it is not extensively practiced. The method needs careful experimentation because the signal levels are low if the usual constraint that the ac amplitude V_{ac} be much less than RT/nF is imposed. This constraint is necessary if the output signal is viewed as an admittance, because the very concepts of admittance and impedance are meaningless unless the ac current amplitude I_{ac} is proportional to V_{ac} . However, this is not a necessary viewpoint. One can measure I_{ac} whether or not it is proportional to V_{ac} and we advocate that amplitudes several times larger than RT/nF be routinely employed.

In this presentation, the findings of a mathematical study [3] of reversible ac voltammetry with an applied ac potential of any magnitude will be reported. A parallel simulation study [4] confirms our findings. It is well known that the voltammetric peak height I_{peak} is proportional to V_{ac} , to the square-root of the frequency, and to the bulk concentration of reactant, when V_{ac} is much smaller than RT/nF . Moreover, the reversible faradaic current shows a phase lag of 45° with respect to the applied ac potential. We find that all of these properties, other than the proportionality to V_{ac} , are preserved even if the latter greatly exceeds RT/nF . Thus, provided that V_{ac} is known, or is kept constant from one experiment to the next, electroanalysis by ac voltammetry remains practicable if the stricture $V_{ac} \ll RT/nF$ is violated. And, of course, a valuable increase in sensitivity and precision accrues from the enhanced signal.

A reversible ac voltammogram, in which I_{ac} is plotted versus a slowly varying E_{dc} is a familiar bell-shaped curve. Interestingly, we have shown that the area beneath this curve remains exactly proportional to V_{ac} , even when I_{peak} is not.

References

1. D.E.Smith *Electroanalytical Chemistry* (ed A.J.Bard), Vol 1, Dekker, New York, 1966
2. A.M.Bond, *Modern Polarographic Methods in Analytical Chemistry*, Dekker, NY, 1980
3. S.O.Engblom, J.C.Myland and K.B.Oldham, *J.Electroanal.Chem.* in press
4. A.M.Bond and D.Gavaghan, *J.Electroanal.Chem.* in press

**ELECTROANALYSIS AT NANOMOLAR AND SUBNANOMOLAR
CONCENTRATION LEVELS BY MULTIPLE SQUARE WAVE VOLTAMMETRY
AT ION-EXCHANGER COATED ELECTRODES**

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The preconcentration capabilities of electrodes modified with thin films of ion-exchange polymers are currently exploited for developing new electroanalytical methods for trace electroanalysis. These analytical performances can be further improved by using the modified electrodes in combination with sensitive pulsed techniques. Recently, a new pulsed technique, named Multiple Square Wave Voltammetry (MSWV), has been introduced. It is based on the principle of repeated addition of the integrated transient currents produced by a multiple potential steps sequence applied at the electrode. MSWV is a multi-pulse technique which implies a combination of a crenelate waveform with a staircase waveform. This perturbation mode is similar to Barker's square wave voltammetry (SWV), but with the difference that, onto each step of the staircase, more than one pair of square pulses of opposing sign are applied.

This communication presents the results of a study aimed to combine the preconcentration ability and selectivity of ion-exchanger coated electrodes with the dramatic improvement of the signal to noise ratio which characterises MSWV. In particular, this presentation will focus on the MSWV trace determination at Nafion coated electrodes of the some redox cations such as CH_3Hg^+ and Eu^{3+} , which are of interest in ecotoxicological and geochemical studies. Optimisation of methods shows that MSWV, in the double differential mode, allows the determination at Nafion coated electrodes of concentrations in the nanomolar and subnanomolar range for the examined analytes. In all cases, the use of MSWV reflects in an improvement in detection limits of 2-3 order of magnitudes with respect to "classical" pulsed techniques such as DPV and Osteryoung-SWV.

VOLTAMMETRIC ANALYSIS OF UNDILUTED ORGANIC LIQUIDSJoanna Gadomska and Zbigniew Stojek

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Several organic liquid compounds in their undiluted states have been examined voltammetrically so far. The first reports on the possibility of obtaining well defined waves of undiluted liquids were given by White et al. New interesting phenomena related to such measurements have been found. Correspondingly, a substantial progress in the mathematical modelling of voltammetric waves of undiluted substances was made. The analytical aspects of voltammetry of undiluted organic liquids are mainly linked to a possibility of rapid determination of water content in the substrates.

Our recent interests were focused on acetonitrile. It gives a cathodic total wave at approximately -3.5 V vs. Pt quasi reference electrode. The height of the wave is apparently transport controlled. The ionic microlayer that is formed at the microelectrode surface at the plateau region is stable in time. The wave is formed only in the presence of a small concentration of the tetra alkyl ammonium cations and not in the presence of the alkali metal cations which cause the precipitation of the ionic liquid at the microelectrode surface. The experimental dependence of wave height on radius of the counterion does not fit the existing theory, since experimental voltammetric wave heights are significantly lower than those calculated. These deviations are interpreted in terms of some extra interactions within the ionic layer which lead to a further decrease in diffusion coefficients of the participating species in the ionic microlayer. In the anodic region the wave plateau can not be reached up to 6 V.

Water dissolved in acetone can be reduced in the potential range just before the total cathodic wave of undiluted acetonitrile. Height of the water wave is in a wide range proportional to water concentration. This allows the determination of water content in acetonitrile by a simple voltammetric procedure.

**A NEW ACCESS TO GIBBS FREE ENERGIES OF TRANSFER OF IONS ACROSS
LIQUID-LIQUID INTERFACES AND A NEW METHOD TO STUDY
ELECTROCHEMICAL PROCESSES AT WELL-DEFINED THREE-PHASE
JUNCTIONS**

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Droplets of polar and nonpolar aprotic solvents containing dissolved electroactive species can be easily attached to paraffin impregnated graphite electrodes. When the electrode with the attached droplet is introduced into an aqueous electrolyte solution, the electrochemical reactions of the dissolved species can be elegantly studied. Provided the droplet does not contain a dissolved electrolyte, the electrochemical reaction will be confined to the very edge of the three-phase junction droplet | graphite | aqueous electrolyte. When a neutral species is oxidized, two pathways are possible: the oxidised species can remain in the droplet and anions will be transferred from the aqueous solution to the organic solvent, or the oxidised species may leave the droplet and enter the aqueous solution. Depending on the nature of the dissolved species, the nature of the organic solvent, the presence or absence of appropriate anions and cations in the two liquid phases, very different reaction pathways are possible. The new approach allows studies of ion transfer between immiscible solvents to be performed with a three-electrode potentiostat. Electrochemical determinations of the Gibbs Free Energies of ion transfer between aqueous and nonpolar nonaqueous liquids are possible, whereas conventional ion transfer studies require the presence of a dissociated electrolyte in the organic phase. The new method considerably widens the spectrum of accessible ions.

ELECTROCHEMISTRY: A POWERFUL ANALYTICAL TOOL IN STEEL RESEARCH

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This presentation is intended to close the gap between fundamental electrochemical research and its application in industry, specifically in the steel industry.

A wide variety of electrochemical techniques and applications are described and discussed. It will be shown that electrochemistry is sometimes the ultimate technique that can compete with the most powerful analytical techniques available nowadays.

Galvannealed coatings are Fe-Zn coatings, mainly applied in the automotive industry for outdoor parts. Amperostatic measurements (coulometry) is until now the only technique that allows the determination of intermetallic Fe-Zn phases of a galvannealed coating by sequential dissolution. The combination of ICP-MS with selective electrochemical dissolution was successfully used to calibrate the coulometric response. Moreover, the developed methodology opened new insights in the understanding of the Fe-Zn electrochemical dissolution reactions. Nowadays, we use coulometry routinely for the semi-quantitative determination of the phase specific coating weight and phase specific coating thickness of the Fe-Zn-intermetallics. The coulometric technique was verified on more than 200 industrial and laboratory simulated samples of galvannealed Fe-Zn coatings.

Potentiodynamic measurements can reveal useful information on the sample surface state or surface reactivity towards oxidation of steel sheets. The surface reactivity of a steel sheet is the ability of the surface to form a uniform, homogeneous and continuous passivation layer that will prevent the material from further oxidation (comparable with the passivation behaviour of stainless steels). A reproducible and sensitive potentiodynamic method was developed to compare the passivation behaviour of steel surfaces. The passivation behaviour of steel sheets only occurs under specific measurement conditions as e.g. the type of electrolyte, pH, temperature, scan rate, etc.

On demand of a steel customer, potentiodynamic measurements were used to predict the surface passivation behaviour of various materials. Based on this electrochemical technique, the thermal oxidation step in the production line could be optimised with respect to temperature and humidity. Electrochemical measurements and corrosion weathering tests give similar results.

As a spin-off, this methodology is now used "off-line" in a steel production step to optimise and control the surface passivation behaviour and to reduce production costs.

For the evaluation of paint systems on metallic samples, electrochemical impedance spectroscopy (EIS) is a powerful technique in the industry of corrosion protection. Most

paint systems on steel sheets have a non-conductive coating with a thickness of typically 20 to 200 μm . Therefore, conventional corrosion study techniques cannot be applied. On the other hand, corrosion weathering simulations are expensive and very time-consuming whereas EIS can give information on the coating characteristics long before visual corrosion reactions are observed.

For the optimisation of a coating system, we used EIS to compare competitive products under standardised conditions. This allowed us to compare different systems as a function of their coating resistance. The speed of water diffusion through the coating seems to be the most critical factor for the drop of the coating resistance. Impedance measurements are now used as a feedback method for the optimisation of various paint coatings on metallic substrates.

Stainless steels cover a wide range of products with one common characteristic: their excellent corrosion resistance. The anti-corrosion characteristics are the result of the very efficient build-up of a surface passivation layer. Nevertheless, the most common stainless steel grades are sensitive to local corrosion phenomena. The Critical Pitting Temperature (CPT) test according to ASTM G150 is a method to evaluate the resistance of stainless steels to pitting corrosion as it is related to the potential independent critical temperature. The critical pitting temperature value is the lowest temperature that results in a stable propagation of the pits on a test surface.

Different stainless steel grades with variations in elemental composition can be evaluated by CPT-measurements. CPT-measurements are a useful tool for the optimisation of the surface specific post-treatment of stainless steel surfaces.

QUALITATIVE AND QUANTITATIVE ANALYSIS OF REACTION PRODUCTS ON LEAD-SULPHURIC-ACID BATTERY ELECTRODES BY COMBINATION OF ELECTROCHEMICAL AND INFRARED SPECTROSCOPIC TECHNIQUES

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The analysis of electrode surfaces of battery electrodes leads to important information about the influence of different parameters like temperature, composition and pH of the electrolyte solution and concentration of dissolved gases on the life time behaviour of electrochemical energy storage systems. In lead-acid battery electrodes the formation and consumption of lead sulphate is the most important reaction during the discharge and charge processes. Due to a complex mechanism which causes an increasing pH value under a dense lead sulphate layer some other lead compounds (monobasic and threebasic lead sulphate, $\text{PbO} \cdot \text{PbSO}_4$ and $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$) can be formed.

Any preparation of the electrodes (e.g. drying) which is necessary before applying special analytical methods may influence the composition of the electrode surface layer. So it is necessary to apply in situ methods to avoid these influences. Good results can be obtained by combination of different electrochemical methods and infrared spectroscopy. This combination gives both qualitative and quantitative information about the composition of electrode surfaces without taking the electrodes out of the electrolyte solution. Coulometric and voltammetric measurements combined with infrared spectroscopic investigations of the electrode surface during the anodic reaction leads to useful calibration curves for quantitative analysis of battery electrodes surfaces.

Some results of applying in situ spectroelectrochemical techniques on the lead - sulphuric acid system like the quantification of the thickness of the lead sulphate layer (the extent of the sulphatation reaction) and the influence of dissolved oxygen on the electrode reactions will be discussed.

ENVIRONMENTAL MONITORING: DISPOSABLE BIOSENSORS OR REPLACEABLE MEMBRANES?

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Biosensor based monitoring of environmental pollutants implies commonly the detection of enzyme inhibitors, i.e. pesticides, heavy metal salts etc. because of the high requirements to their detection limits. The analytical signal assumes in this case the decay of a biosensor response and hence the number of series measurements is limited. The application of specific reactivators complicates the use of biosensors especially in field conditions or as recognition elements in autoanalyzers. In this respect the practical application of biosensors for environmental monitoring takes two paths. One of them involves the development of cheap single use biosensors based on the microfabricated sensors with an enzyme directly immobilized on the active surface without any carrier. The second approach is based on the standard measurement devices with replaceable enzymatic membranes closely attached to the electrode surface. Both approaches demonstrate different advantages and weak points discussed in this report. Various cholinesterase based biosensors have been developed and examined for the detection of organophosphorus pesticides in fresh waters and plant origins. Butyrylcholinesterase from horse serum (Serva) was immobilized on the Nylon (Hybond, Amersham) and cellulose nitrate (Sartorius) membranes and directly on the surface of Sb potentiometric electrode and epoxy-carbon planar thick film potentiometric electrodes. In the latter case upper covering layers of albumin or Nafion were also used for the alteration of membrane properties. For the pesticide detection, the biosensors were incubated for 10 min. in diluted extracts containing of less than 20% of organic solvent (acetone, acetonitrile, ethanol). Then the relative decay of the response (degree of inhibition) was determined as a measure of pesticide content. Biosensors with replaceable membranes make it possible to perform up to 10 measurements per hour and up to 15 measurement with the same membrane cut. The reproducibility of the response did not exceed 2% for potentiometric and 3% for amperometric detection systems. The following detection limits of pesticides were obtained for the trace amounts of pesticides in rice, rye, wheat: Malathion 0.15 (Nylon) 0.12 (cellulose nitrate), Co-Ral 0.07 (Nylon) 0.10 (cellulose nitrate), Chloropyrifos 0.05 (Nylon) 0.08 (cellulose nitrate) mg kg⁻¹. Disposable biosensors showed better sensitivity toward Co-Ral and Chloropyrifos. Meanwhile their sensitivity toward Malathion and Trichlorfon was 1.5-2.0 lower than that of biosensors with replaceable membranes. Disposable biosensor demonstrate at least the same life time when leaved in buffer solution (1.5-2 weeks at room temperature) but much shorter storage time in dry conditions as compared with enzymes immobilized on commercial supports (2-3 and 15-20 weeks, respectively). The influence of macrocomponents of biomatrix on the operational and analytical characteristics of biosensors and the ways of stabilization of biosensor response during their storage in various conditions are discussed.

GRAPHITE-TEFLON-HRP COMPOSITE ELECTROCHEMICAL BIOSENSORS FOR THE SCREENING OF PHENOLIC COMPOUNDS

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Amperometric biosensors based on the enzyme tyrosinase have been widely used for the detection of phenolic compounds. Nevertheless, they are restricted to the monitoring of phenolic compounds with at least one ortho-position free. With the aim of extending the number of these compounds that can be detected, we have developed a peroxidase biosensor. This enzyme exhibits a relatively low specificity towards electron-donor substances as the phenolic compounds are, and possesses a high stability and efficiency. Furthermore, the peroxidase biosensor can be complemented with biosensors of tyrosinase for the detection of some of these compounds which do not respond to HRP or show a low sensitivity with this enzyme.

The mechanism of the HRP catalysed reactions in the presence of hydrogen peroxide and a electron-donor compound is of the "ping-pong" type. The addition of H_2O_2 to the working solution is needed, and the monitoring of the enzymatic reaction is carried out by the electrode reduction of the generated phenoxyl radicals.

On the other hand, the use of composite graphite-Teflon electrodes where the enzyme is physically included into the matrix has demonstrated to give rise to robust and efficient biosensors whose surface can be easily regenerated by polishing. In this communication, results obtained with graphite-Teflon-HRP electrodes for amperometric detection of 18 phenolic compounds, most of them included in the EPA pollutant list, are presented.

The working variables such as H_2O_2 concentration, pH and applied potential were optimised, and a study on the stability of the composite bioelectrode was carried out. Moreover, kinetic constants of the catalytic reactions were calculated. We verified that the sensitivity of the biosensor with respect to the different phenolic compounds studied depended mainly on the relative position of the substituents with respect to the OH group in the benzenic ring.

Finally, the analytical characteristics (range of linearity and limit of detection) have been evaluated for the tested compounds, being adequate for the determination of phenolic compounds in industrial waste water. These detection limits are better in most cases than those found in the literature with other biosensors. Nevertheless, since better detection limits can be obtained for some phenolic compounds with a tyrosinase electrode, both enzymes have been coimmobilized into the composite matrix to improve sensitivity.

**POLAROGRAPHIC AND VOLTAMMETRIC DETERMINATION OF
CARCINOGENIC NITRO AND AMINO DERIVATIVES OF POLYCYCLIC
AROMATIC HYDROCARBONS**

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Nitro and amino derivatives of polycyclic aromatic hydrocarbons are well known chemical carcinogens which should be carefully monitored in our environment. So far, mostly HPLC methods were used for these purposes [1] while polarographic and voltammetric methods are used less frequently [2]. Therefore, we have investigated the use of modern polarographic and voltammetric techniques (namely differential pulse polarography, differential pulse voltammetry, adsorptive stripping voltammetry and HPLC with electrochemical detection) for the determination of selected carcinogenic nitro and amino derivatives of naphthalene, anthracene, fluorene, fluoranthene and biphenyl. Optimum conditions have been found for the determination of nanomolar or subnanomolar concentration of nitro derivatives using mercury electrodes (DME or HMDE) and for the determination of submicromolar concentration of amino derivatives using carbon paste electrodes. HPLC with electrochemical detection using the newly developed platinum tubular detector is suitable for the determination of submicromolar concentrations of amino derivatives. The selectivity of all methods can be improved by preliminary separation using liquid - liquid or solid phase extraction. Newly developed methods were used for the determination of model nitro derivatives in river water and for monitoring the efficiency of the destruction of carcinogenic nitro and amino derivatives.

REFERENCES

1. Cvacka J., Barek J., Fogg A.G., Moreira J.C., Zima J.: *Analyst*. 1998, 123, 9R
2. Barek J., Cvacka J., Mejstřík V., Muck A., Zima J.: *Crit.Rev.Anal.Chem.* 1999, 29,81-83

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HIGHLY SENSITIVE AMPEROMETRIC GAS SENSORS BASED ON METALLIZED ION-EXCHANGE MEMBRANES

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Platinum or gold electrodes, which have been deposited by chemical reduction onto solid polymer electrolyte (SPE) membranes such as Nafion, are employed. The membrane serves as mechanical support for the electrode and a conductive bridge to the internal filling solution and the counter and reference electrodes. The approach is similar to SPE-fuel cell technology where also highly efficient gas electrodes are desired. In contrast to earlier amperometric gas sensors, the working electrode is directly exposed to the gas phase and the analyte does not have to diffuse through a membrane. Higher sensitivities, better detection limits and faster responses are thus attainable for electroactive species.

The sensing of ethylene, acetylene, ethanol, acetaldehyde and sulphur dioxide has been reported previously and detection limits as low as 1 ppb (v/v) have been achieved. Gases presently under investigation are ethylene oxide, nitrogen oxide, nitrogen dioxide, methane and formaldehyde.

A survey of research findings will be given. The behaviour of the sensors with regard to operating parameters such as gas flow rate and the humidity of the gas stream will be discussed. Striking differences were observed for the species studied and in some cases current limitation by the reaction kinetics rather than the usual diffusion control was found. A further important criterion is the selectivity and it will be shown that by judicious optimization of such variables as the applied potential, the choice of the electrode metal, the composition of the internal electrolyte solution, and the use of chemical trapping methods good selectivities can be obtained for most of the electroactive gases.

Poster Contributions

Session A

DETERMINATION OF IONS IN WOOD PULP BY ISES

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Ion-selective electrodes (ISEs) provide an analytical tool that permits the specific and precise determination of a number of analytes, especially in clinical and environmental chemistry. The application of ISEs in process analytical chemistry is limited due to insufficient properties of the electrodes and lacking protocols for determination of ions in wood pulp matrices. In this research the optimization of selected ISEs was undertaken in view of their application in on-line monitoring of potassium, sodium, calcium, pH and chloride in wood pulp.

ISEs obtained from Orion (USA), chloride ISE from Volta (Russia), as well as home-made ISEs with polymeric membranes of different compositions were used. The performance of the ISEs was checked both in model solutions, covering the typical ion concentration ranges in the pulps, and in pulp samples taken from an industrial pulp production plant. Direct potentiometry and a standard addition technique were used for determination of ions.

Reliable results in native pulps and in pulp filtrates were obtained both by direct potentiometry and by standard addition. However, some differences between free ion concentration determined by ISEs and total substance concentration measured by ICP-AES were observed, especially for calcium. These differences were tentatively attributed to the complexation of ions by some constituents of the pulps.

By comparing the performance of different ISEs in the same pulp samples, the most promising sensors suitable for application in wood pulp were selected. These are: (i) Orion RossTM with glass membrane for pH-measurements, (ii) K⁺-ISE based on valinomycin with the PVC membrane plasticized with bis(butylpentyl)adipate (BBPA), (iii) Na⁺-ISE based on 4-tert-butylcalix[4]arene with BBPA as a plasticizer and ETH 500 as a background electrolyte, (iv) Ca²⁺-ISE based on ETH 1001, plasticized with o-nitrophenyloctyl ether and containing ETH 500, and (v) Cl⁻-ISE based on AgCl.

Further efforts will be devoted to the development of solid-contact ISEs with the optimized membranes, and the possibility of measurements at elevated temperatures.

DIFFERENTIAL ENFET-BASED SENSOR CHIP WITH HIGH STABILITY IN THE LONG TERM

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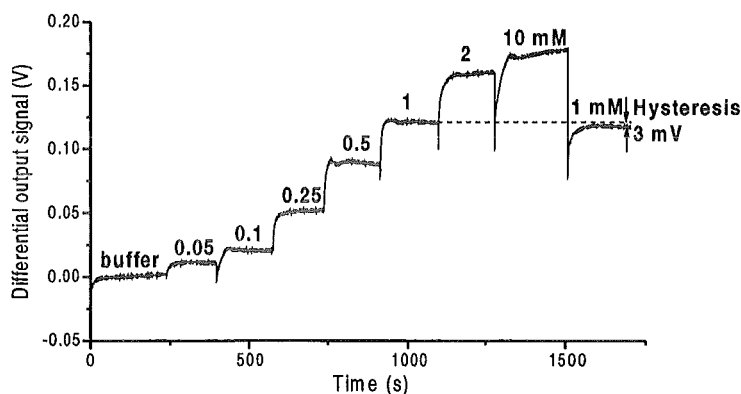
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For many fields of application (drug control, clinical laboratories, food control, etc.) a rapid and inexpensive analysis method that is based e.g. on chemical microsensors is desirable. Such sensors should possess a high stability in the long term as well as a low detection limit. In principal, so-called EnFETs (enzyme FETs) on the basis of the enzyme penicillinase (PenFET) offer this potentiality. However, the performance of such biosensors mainly depend on the intrinsic EnFET characteristics.

In this report we demonstrate that by choosing optimized conditions, such as a Ta₂O₅ gate as the pH transducer material, an appropriate working buffer and a simple enzyme immobilization method, a highly long-term stable penicillin sensor with a low detection limit could be realized. The sensor is operated in a PenFET/pH ISFET differential set-up in order to compensate disturbing factors like the pH variation of the bulk solution and the temperature-induced drift. A typical sensor response of the EnFET-based dual chip to different penicillin concentrations is given in the figure (see below).



The developed biosensor shows a stability in the long term of more than 1 year, a sensitivity towards penicillin of about 120 ± 10 mV/mM in the linear concentration range from 0.05 mM to 2 mM, a hysteresis of less than 4 mV, and a detection limit of about 5 μ M.

**POTENTIOMETRIC STUDY OF THE COMPLEXATION OF IONS
OF BARIUM, ZINC AND LEAD WITH ISOMERIC NAPHTHALENE
SULFONATE IONS IN AQUEOUS ACETONE SOLUTIONS**

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When the rates of processes in the inner and outer coordination sphere are not too low and are commensurable, the experimental methods for determining the stability of complex compounds of labile ions of metals with anionic ligands usually give information on the sum of outer and inner sphere complexation processes, so that the problem of their separation is difficult.

Metal naphthalene sulfonates comprise a broad group of compounds, and their great practical importance has stimulated the investigation of their properties. The growing interest in the utilization of the electron-donor properties of these anions in analytical chemistry prompted the study of the special features of their complexation with metal ions, particularly the isovalent ions of barium, zinc and lead.

In the present work the complexation of the ions of barium, zinc and lead with isomeric naphthalene sulfonates ions in water and water-acetone solutions has been investigated by potentiometric method, using Hg/Hg EDTA indicator electrode. It has been shown that the stability of the complexes varies along the series $Ba > Zn > Pb$, the complexes with electron-acceptor substituents into the naphthalene ring results in increase in the stability of the complex in comparison to the unsubstituted naphthalene sulfonates. The contribution of the outer sphere interaction to the complexation equilibrium in the first and second stages of the process has been evaluated. The greater stability of the outer sphere complexes in comparison to the inner sphere complexes has been demonstrated. The stability constants of the complexes of all the types have been evaluated.

PHTHALOCYANATES OF ALUMINIUM(III), TIN(IV) AND COPPER(II) AS ACTIVE COMPONENTS IN SALICYLATE-SELECTIVE ELECTRODES

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Among a variety of metal-containing compounds applied in anion potentiometric sensors porphyrin metallocomplexes are likely to be the widest class of ionophores. The phthalocyanines are synthetic analogues of the biologically important porphyrins and offer reactivity similar to the porphyrins, yet are more resistant to chemical decomposition and more easily accessible. Metallophthalocyanines are used extensively in the development of chemical sensors, but only a few ion-selective electrodes based on these complexes are known [1-3].

Potentiometric response of plasticized polymeric membranes doped with tetrakis-tertbutylphthalocyanates of Al(III), Sn(IV), Cu(II) were studied toward salicylate in dependence from active compound content, plasticizer nature and the presence of lipophilic ionic additives. All the reagents provide near-Nernstian response to salicylate within a broad concentration range, but the lowest detection limit ($1.3 \times 10^{-5} \text{ M}$) is achieved with the use of $\text{Pc}^{\text{I}}\text{SnCl}_2$ membrane carrier. It should be noted that the parameters of response for membrane based $\text{Pc}^{\text{I}}\text{Cu}$ deteriorate noticeably within three days (the slope finally falls to $42 \pm 2 \text{ mV/dec}$, detection limit is $1.3 \times 10^{-4} \text{ M}$) and keep constant for at least further two weeks. It is shown that the Al(III) and Sn(IV) complexes provides the high selectivity to salicylate which deviates significantly from Hofmeister series. The different mechanisms are suggested for studied metallophthalocyanates in PVC-membranes on the basis of influence of lipophilic additives.

References

1. Li, J.; Pang, X.; Yu, R. *Anal.Chim.Acta.* **1994**, 297, 437.
2. Li, J.; Pang, X.; Yu, R. *Talanta.* **1995**, 42, 1775.
3. Shvedene, N.; Belchenko, N.; Starushko, N.; Tsherbakova, M.; Tomilova, L.; Pletnev, I. *Vestnik MGU, ser.2. Khimija.* **1999**, 40, 3, 160.

POTENTIOMETRIC AND COULOMETRIC DETERMINATION OF THIOLS

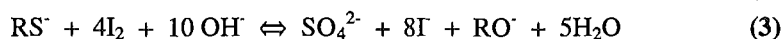
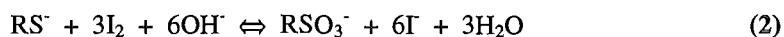
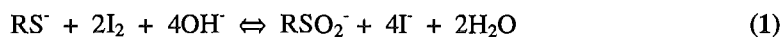
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New methods for the determination of thiols involving their reaction with iodine in an alkaline medium are presented. Two techniques of determination were applied: the volumetric titration with potentiometric end-point detection and the coulometric titration using biamperometric end-point detection.

In acidic and neutral medium the reaction between studied thiols and iodine was very slow and iodimetric titration was impossible. In an alkaline medium the reaction rate increases and the stoichiometry of reaction changes. The number of electrons transferred in the reaction of 1 mol thiol depends on the kind of compound and conditions of tested substances determinations.

The following equations of oxidation of thiols by iodine in alkaline medium are suggested:



Conditions of reactions courses were defined and determinations of different thiols such as 2-mercaptobenzothiazole (1), 2-mercaptobenzimidazole (1), thioguanine (1), 1-phenyl-2-mercaptotetrazole (2), 2-mercaptobenzoxazole (3) and 5-phenyl-1,3,4-oxadiazole-2-thiol (3) will be presented. Elaborated methods were applied for determination of thioguanine in drug.

References:

1. W. Ciesielski, R. Zakrzewski, A. Krenc and J. Zielińska, *Talanta*, **47**, 745-752 (1998)
2. W. Ciesielski and A. Krenc, *Pharmazie*, **53** (11), 801-802 (1998)

POTENTIOMETRIC DETERMINATION OF THERMODYNAMIC IONIZATION CONSTANTS OF 5,5-DYMETHYLHYDANTOIN AND 1-HYDROXI-5,5-DYMETHYLHYDANTOIN

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The domestic use of fresh waters requires special treatments. One of the main steps in this procedure is disinfection. Chlorine gas and some of its derivatives have been traditionally used for this purpose. However, it has been proved that these agents can react with the organic matter present in natural waters producing impurities and toxic products which can dangerously accumulate in the environment [1]. In an effort to avoid any risks for human health or environmental pollution, substances as N-halogenated compounds have been used as disinfectant agents. New compounds are continuously investigated in this field and it is to be noted the importance of halogenated derivatives of hydantoins.

Since acid-base properties [2] of this type of compounds result of great interest in order to establish their biological activity, we have considered the study of such properties relevant. We have selected two simple compounds from the hydantoin derivatives so that in further studies, halogenation reactions can be established. The compounds used in the present work were: 5,5-dimethylhydantoin (I) and 1-Hydroxi-5,5-dimethylhydantoin (II). The ionization constants of both samples were determined using the potentiometric technique [3] (with a combined glass electrode) in the ionic strength range 10^{-3} -1 M KNO_3 . Different models [4] were applied to obtain the thermodynamic ionization constants: Guggenheim (model 1), Pitzer (model 2), etc.

MODEL	SAMPLE	pK($\pm$ std.dev)
1-2	(I)	9.33(0.01) - 9.32(0.01)
1-2	(II)	9.166(0.015) - 9.14(0.01)

References

1. R.G. Tardiff, G.P. Carlson, V. Simmon. Water Chlorination. Environmental Impact and Health Effects. Vol 1, 195-209. R.L. Jolley etc. Eds. Ann Arbor Science (1975)
2. L.W. Pickett, M. McLean. J. Am. Chem. Soc. 61, 423-425 (1982)
3. M.E. Sastre de Vicente. Current Topics in Solution Chemistry 2, 157-181 (1997)
4. S. Fiol, I. Brandariz, R. Herrero, T. Vilariño, M.E. Sastre de Vicente. Ber. Bunsenges. Phys. Chem. 98(2), 164-171 (1994)

POTENTIOMETRIC DETERMINATION OF PITZER PARAMETERS FOR SODIUM BENZOATE AT 298.15 K

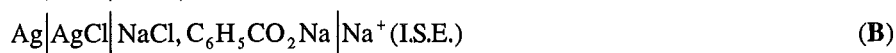
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Sodium benzoate is widely used in industry, and its thermodynamic properties are still not well known. Pitzer theory ^(1, 2) has been applied to the activity coefficients calculation of many salts in aqueous solutions with ionic strength up to near saturation. The theory is based on a semi-empiric equations system for describing the non-ideal behaviour of electrolyte solutions. The application of the Pitzer theory demands the knowledge of specific parameters for the electrolytes⁽³⁾. However, sodium benzoate parameters are not available in the literature.

In this work, potential differences on cells A and B were used to evaluate experimental sodium chloride mean activity coefficients of pure aqueous solutions (cell A) and mixed solutions of sodium chloride and sodium benzoate (cell B).



Theoretical Pitzer equation for $\ln \gamma_{\text{NaCl}}$ of sodium chloride in the electrolyte solution of cell B was used to fit the experimental data for $\ln \gamma_{\text{NaCl}}$ and the specific parameters for sodium benzoate were obtained by linear regression. This method has already been used in the determination of Pitzer parameters values of other salts ^(4, 5). The values thus obtained are close to those already published for other carboxylic acid salts ⁽³⁾.

REFERENCES

1. Pitzer, K.S.; Mayorga, G.; J. Phys. Chem., 77, 2300 (1973).
2. Pitzer, K.S.; Mayorga, J. Solution Chem., 3, 539 (1974).
3. Pitzer, K.S.; "Ion interaction approach: Theory and Data Correlation" in Pitzer, K.S. (editor) "Activity coefficients in electrolyte solutions", 2nd edition, CRC Press, Boca Raton, USA, 1991, pg 75-153.
4. Mendonça, A.J.G. de, "pH values of standard solutions using Pitzer theory", PhD thesis University of Beira Interior, Covilhã, Portugal, 1998, pg 63-97.
5. Lanier, R.D.; J. Phys. Chem., 69, 3992 (1965).

PROCESSIBLE POLYANILINE AS AN ADVANCED POTENTIOMETRIC PH TRANSDUCER FOR BIOSENSOR APPLICATIONS

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The measurement of the solution pH is an important task required for clinical diagnostics, environmental and industrial control, and various branches of modern science and technology. A particular case of application of the pH transducers is the development of potentiometric biosensors. Polyaniline represents one of the most promising materials for pH sensing. The use of polyaniline for development of potentiometric biosensors with improved sensitivity was first reported by our group [1]. Recent investigations on the processing of polyaniline (PCPAn) [2] have provided new opportunities to simplify the procedure of preparing PAn-modified electrodes. An advanced potentiometric pH transducer based on processible polyaniline (PCPAn) is reported. Both glassy carbon and screen-printed carbon electrodes modified with PCPAn by dip-coating exhibited a fully reversible potentiometric response of approximately 90 mV/pH over the range from pH 3 to pH 9. Such significantly higher potentiometric response of PCPAn modified electrodes compare to existing devices is explained on the basis of the thermodynamics of polyaniline redox reactions. The PCPAn based pH transducers exhibits both good operational stability and prolonged shelf life, and displays a negligible response towards the single-charged cations. The new thick-film pH transducer was employed for designing a potentiometric biosensor for urea.

References

- [1] Karyakina, E. E.; Neftiyakova, L. V.; Karyakin, A. A. *Anal. Lett.*, 27, 1994, pp. 2871-2882.
- [2] Cao, Y.; Qiu, J. J.; Smith, P. *Synth. Metals*, 69, 1995, pp. 187-190.

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POTENTIOMETRIC PERFORMANCE AND INTERFACIAL KINETICS OF NEUTRAL IONOPHORE BASED ISE MEMBRANES IN INTERFERING ION SOLUTIONS BEFORE AND AFTER CONTACT WITH PRIMARY IONS

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It is known that ion-selective electrodes (ISEs) do not provide Nernstian response in pure solutions of electrolytes containing highly discriminated ions. However, it was shown recently [1] that the ISEs may give a full Nernstian response in pure solutions containing interfering ions prior to the first contact with primary ions. After being in contact with the primary ions, the ISEs lose the Nernstian response to the interferences [1].

The aim of this work was to study whether the ISE membrane/solution interface reactions are reversible both for primary and for interfering ions, and whether the reversibility depends on the treatment of ISEs.

We studied the potentiometric response and the electrochemical impedance spectra of thin (40 µm) PVC based ion selective membranes containing Ca²⁺ ionophore ETH 1001 and Na⁺ ionophore 4-tert-butylcalix[4]arene, before and after the contact with CaCl₂ and NaCl solutions respectively. The membranes included potassium tetrakis(p-Cl-phenyl) borate, thus being initially in potassium form. The internal electrolyte was always the same as the electrolyte outside. The concentration of the inner solution was kept constant (0.01 M) in potentiometric experiments, but the outer solution concentration varied within the range 0.1 – 0.001 M. Impedance measurements were carried out in a symmetric cell: the concentrations of inner and outer solutions were the same. The electrodes were conditioned for 2 days and then calibrated in pure solutions of interferences: NaCl and KCl for Ca²⁺-ISEs, and KCl and CaCl₂ for Na⁺-ISEs. Nearly Nernstian potentiometric responses were obtained. Impedance spectra were then recorded in the same solutions. Then the ISEs were equilibrated with their primary ions. Potentiometric response and impedance spectra were recorded in pure CaCl₂ and NaCl. After the contact with primary ions the measurements in the interfering electrolytes were repeated. The ISEs responses to the interfering ions became rather sub-Nernstian, while the impedance spectra remained practically the same.

The results suggest that the membrane/solution interface reactions are reversible both for the primary and the interfering ions regardless of the treatment of ISEs.

CONSTANT-CURRENT-MODE LAPS FOR DETECTION OF PENICILLIN

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The light-addressable potentiometric sensor (LAPS) is a semiconductor-based chemical sensor with an electrolyte-insulator-semiconductor (EIS) structure. In this structure, the width of the depletion layer formed at the insulator-semiconductor interface varies in response to the surface potential. A dc bias voltage is applied to the EIS structure, and the sensor is illuminated with a modulated light. By measuring the ac photocurrent, the variation of the depletion layer can be detected.

In this study, we constructed the constant-current-mode LAPS, the so-called CLAPS, in which a feedback loop maintains the photocurrent at a constant value by adjusting the bias voltage. The variation of the bias voltage directly corresponds to the change of the surface potential. Thus, the constant-current mode is suitable for recording of a dynamic process.

The CLAPS was applied to the detection of low-concentration penicillin by measuring the pH change in an enzymatic reaction. The pH-sensitive insulating layer of Ta₂O₅ was deposited on the *p*-type Si substrate by the pulsed laser deposition (PLD) technique, and penicillinase was immobilized on the sensing surface by means of physical adsorption.

Figure 1 shows an example of the sensor response to various concentrations of penicillin. The pH change is detected even at low concentrations down to 5 μ M. The details of the sensor system and its performance will be reported.

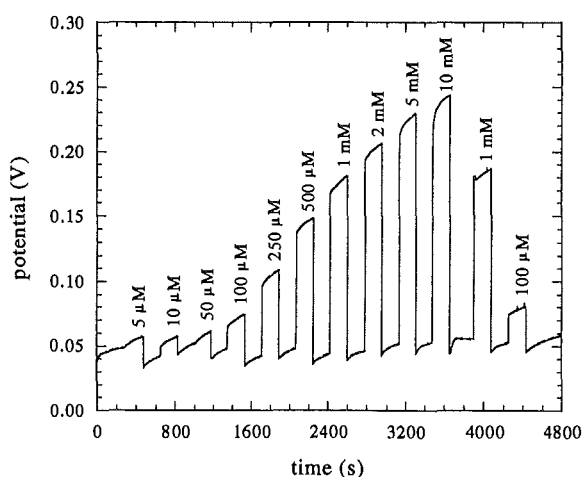


Fig.1. Detection of penicillin by the constant-current-mode enzyme LAPS.

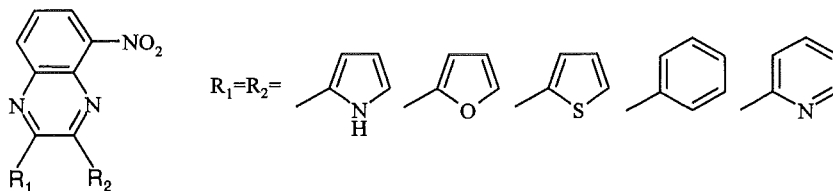
ELECTROPOLYMERIZED FILM BASED ON 2,3-DIPYRROL-2'YL-5-AMINOQUINOXALINES AS NOVEL SENSOR FOR ANION RECOGNITION

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Electropolymerization of aromatic and heteroaromatic compounds, leading to anodic deposition of films, offers new possibilities development of sensor system. In this connection, the 5-nitroquinoxalines modified in 2, 3-position by pyrrole, pyridine, furan, thiophene, benzene units represent interesting material for the development of novel sensor system. Our task was to (i) find the conditions of electropolymerization of 5-nitroquinoxaline systems; (ii) understand the mechanism of polymerization; (iii) study potentiometric characteristics obtained polymerized films.



The electropolymerization of 2,3-dipyrrol-2'-yl-5-aminoquinoxaline was carried from mixture CH₃COOH - 1M H₂SO₄ (95+5 volume %) by repeatedly cyclic scanning the platinum electrode potential from -0.3 to +1.25 V vs Ag/AgCl saturated electrode at 50 mV/s. The comparing of Raman spectra of monomer and polymer quinoxalines with various units at 2,3-position indicated that the electropolymerization may proceed both *via* pyrrole (for pyrrole derivative) and aminophenyl units (for other derivatives). Finally, the high potentiometric selectivity of the polymerized films derived from 2,3-dipyrrol-5-aminoquinoxaline was observed towards H₂PO₄⁻, HSO₃⁻, I⁻, salicylate and benzoate anions.

Acknowledgment

Financial support from Czech Grant Agency (grants No. 203/97/1099 to V.K.), the Ministry of Education of Czech republic (grant VS 97135 to V.K.) is gratefully acknowledged.

INVESTIGATION OF THE HYDROPHOBIC EFFECT IN DNA-SARFACTANT INTERACTION BY ION SELECTIVE MEMBRANE ELECTRODE

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DNA surface has the anionic nature and its interaction with cationic surfactants is very important, specially in gene transfer techniques. In this study, the interaction of DNA with trimethyl ammonium bromide derivatives, such as dodecyl-, tetradecyl- and hexadecyl-

trimethyl ammonium bromide (DTAB, TTAB and HTAB, respectively) were investigated. The mechanistic study of DTAB binding to calf thymus DNA was performed by ion selective membrane electrode, at 27 and 37°C in the presence and absence of NaCl. The binding constants and free energy of the reactions were determined by Wyman-Jones theory, from the binding isotherm, and the enthalpy of binding calculated using van't Hoff equation. The overall enthalpy changes of interaction determined by isothermal titration calorimetry (ITC) and the enthalpy of unfolding calculated by subtracting of binding enthalpy from the overall enthalpy. Comparison of these results with the spectropotometric one, indicated that the electrostatic interactions were dominant and caused the DNA denaturation. DNA interaction with TTAB and HTAB, and also comparison of the results with DTAB, shown DNA denaturation at lower concentration of surfactant with higher hydrophobic tail. It indicated that however the electrostatic interactions are the main effect in DNA-surfactant interaction, but the hydrophobic contributions are accompanied with the former.

LITHIUM ION SELECTIVE GLASS ELECTRODES

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Glass electrodes (GEs) with membranes of glass systems $\text{Na}_2\text{O}(\text{Li}_2\text{O}) - \text{Al}_2\text{O}_3 - \text{SiO}_2$ and $\text{Na}_2\text{O}(\text{Li}_2\text{O}) - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$, being high selective to Na^+ , are well known and widespread. Attempts to reach high Li^+ -selectivity in neutral solutions for GEs, made of Li_2O -containing glasses of these and some other silicate systems, were not successful. The most reached selectivity is described with K_{NaLi} value about 5. The troubles are explained by the greater mobility of the Na^+ ions (comparing to Li^+ ions) in a silicon-oxygen surroundings of aluminium-oxygen tetrahedra [1].

Glasses of non-silicate systems, in particular alkali phosphate ones, are perspective to obtain GEs with higher Li^+ selectivity, but some of them have low chemical durability in water solutions and low conductivity [2]. Our attention was drawn by the glasses of $\text{LiF} - \text{Al}(\text{PO}_3)_3$ system containing 75 - 85 mol % LiF , having high Li^+ ion conductivity and sufficient chemical durability [3]. E.g., the GEs of glass with 80% LiF show the Nernstian Li^+ response in the region of LiCl concentration $1 - 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, LLD $3 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$. They are characterized by K_{NaLi} value about 20, i.e. Na^+ does not affect Li^+ response up to 6:1 ratio. Their sensitivity to H is low. Transition regions of an electrode potential between Li^+ and Na^+ responses and between Li^+ and H^+ responses are correctly described with the Nicolsky equation, what enlarges the possibility of the GEs.

The studies with other glasses of this system and the mechanism of their interaction with water solutions are in progress.

References

1. A.A. Belyustin and E.D. Bagandova// Sens. Actuators B. 1994. V. 18 -19. p. 387.
2. T.I. Kochetova and V.S. Bobrov// Russian J. Appl. Chem. 1994. V.67. p. 1973.
3. A.A. Pronkin, I.A. Sokolov, A.V. Narayev, a.o.// Glass Phys. and Chem.. 1996. V.22. p.524.

THE DEVELOPMENT OF GLASS ELECTRODE THEORY BY B.P. NICOLSKY AND HIS SCHOOL (TO THE 100TH ANNIVERSARY OF B.P. NICOLSKY)

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Since 1937, when BP has published his equation, which in general form can be written as $E = E^O + (RT/F)\ln(a_i + K_{ij}a_j)$ (1), this equation came to be the most usable one in the papers dealing with glass (GE) and other ion-selective electrodes (ISE).

As applied to GE, the theory has passed through some stages: "simple theory" (BP, 1937); "generalized theory" [the 1st variant (BP, 1953); the 2nd variant (BP & Shultz, 1962-63)] At all these stages the GE potential was considered as a phase-boundary one, and K_{ij} as ion-exchange equilibrium constant K_{ij}^{ie} . The dependence of the GEs properties on glass composition was treated on this basis (Shultz, a. o., 1963-67, G. Eisenman, 1965-67).

The next stage was the idea that GE potential is the membrane one, consisting of two phase-boundary (at two glass/solution boundaries) and two diffusion (in altered surface layers) potentials (Eisenman & Carreman, 1962; Stephanova, Shultz & BP, 1963). The K_{ij} value took the sense of a selectivity coefficient, consisting of energetic and migration factors: $K_{ij} = K_{ij}^{ie}((U_j/U_i))$ (2) (U_k are the ion mobilities in glass surface layers). The correct conjugation of both types of potentials turned out to be possible only in framework of the "simple" (not the "generalized") theory. The approximate solutions for the second case were proposed by Buck (1974), Morf (1979, 1985), Shultz & Belyustin (1984). The ideas of the effect of ion-transport-in-membrane mechanism on the GE function selectivity (Shultz & Stephanova, 1970-78) were of a great importance.

The studies of glass surface layer composition (Boksay, et al., since 1964, Baucke, since 1971, Belyustin, Ivanovskaya, et al., since 1975) allowed to confirm the membrane potential conception, to interpret the dynamics of the GE potentials (Belyustin, et al., 1980). The multi-layer model of glass electrode was created (Belyustin, 1980, 1999). The migration factor was used to elucidate some peculiarities in the dependence of the GE properties on glass composition (Belyustin & Shultz, 1996).

The dissociation mechanism of the GE response and interpretation of diffusion potential, proposed by Baucke (1994, 1996), is very valuable for GE theory. In my opinion, the contradiction with Nicolsky theory, underlined there, is seeming. In some other cases the criticism relative to Nicolsky theory is based on misunderstanding and disregarding of facts.

PREDICTION OF POTENTIALITIES AND PRACTICAL USE OF DITHIOPHOSPHORIC ACID HIGH-MOLECULAR DERIVATIVES IN POTENTIOMETRIC TITRATION OF NICKEL, COBALT AND ZINC

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Dithiophosphoric acid derivatives form difficulty soluble chelates with sulfide forming metal ions. Metal dithiophosphates stability increase with a lengthening of radical of the reagent alkyl derivatives. The reagent low-molecular derivatives form stable chelates only with Hg^{2+} , Ag^+ , Cu^{2+} , Pd^{2+} , Bi^{3+} , Tl^{3+} ions. The reagent high molecular (beginning from dioctyldithio-phosphate) form stable complexes with more than 20 metal ions. They can be used for potenti-ometric titration of nickel, cobalt and zinc ions. Ionic products of 20 sulfide forming metal ions with ten dithiophosphoric acid alkyl derivatives (from dimethyl to didecyl) have been de-termined by us [1] for the revealing of possibility of use this class reagents as potentiometric titrants. Using ionic products and degree of individual substances reaction of metal ions we car-ried out of prediction of potentialities of listed reagents use for potentiometric titration of nickel, cobalt and zinc [2] and prognosis of selectivity of each ion determination and possibility of ions mixture titration on the degree of two-component mixture[3]. This prediction is con-firmed completely by experiment. All the potentiometric measurements have been carried out with silver indicator electrode and chlorine-silver reference electrode. The procedures possess high selectivity. Nickel ions can be titrated by alkyl derivatives beginning potassium dioc-tyldithiophosphate, cobalt ions by potassium dinonyldithiophosphate and the following de-rivatives, zinc ion by potassium didecyldithiophosphate and subsequent derivatives.

References

1. Artjukhova N.N., Chebotarev V.K., Marjanov B.M. *Izv. Vuzov. Khimia i khim. tekhnologia*. 1988. v.31, f 9, p.29-32.
2. Chebotarev V.K., Kraev V.K., Voronkina I.V., Y.Iljina / *Talanta*. 1998.47, p.1043-1051.
3. Chebotarev V.K., Kraev V.K., Voronkina I.V. *Asianalysis IV Abstr. Fukuoka, Japan*. 1997. H. 173-2P83.

SELECTIVE REDOXMETRY FOR OXIDANT'S ANALYSES (ACTIVE CHLORINE, OZONE, HYDROGEN PEROXIDE, MOLECULAR OXYGEN)

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Analytical methods for oxidants based on iodometry are widely used in analytical chemistry. For this reason it's important to develop a study of homogeneous and heterogeneous redox reactions related to iodine-iodide system, and a role of an indicator electrode material.

The solutions of $J^{0,1-}$ redox system is well known to modify a surface of Pt electrodes. As a result, the electrodes take on a pronounced selectivity to components of $J^{0,1-}$ redox system in comparison with others. It was found (Pisarevsky et al 1992) that basis of this selectivity is a sharp decrease (of 2 and more orders of magnitude) in the exchange current for Pt electrode with modified surface, in solutions which contained different redox-systems: $Fe^{3+,2+}$, $Ce^{4+,3+}$, O_2/H_2O and others. Whereas the exchange current for $J^{0,1-}$ system almost isn't changed. We can quantitatively characterize the redox selectivity by a selectivity coefficient $K_{J^0,i}$; it's value reaches $10^{-4}+10^{-5}$ and is comparable with the best ones for ion-selective electrodes.

Experimentally was found that Nernst equation is realized up to iodine concentration $\sim 10^{-6}$ M in "pure" solutions of redox-system J_3^-/J^- , pH 2.5-4.5 and KI $\sim 10^{-2}$ M without protection of a cell from the atmospheric oxygen. Deviation of $E-\lg[J_2]$ function from linear at lower concentration range to a considerable extent is caused by impure iodine, and that's why a reversibility violation of the indicator electrode is appeared in solutions where $[J_2] < 10^{-6}$ M [1].

Potentiometric methods for analyses of active chlorine, ozone, hydrogen peroxide and molecular oxygen were developed. The best accuracy, technical simplicity and good determination's precision were reached by a coulometric way of a standard addition of iodine in the cell, without division space into cathode and anode parts. This analytical scheme became to be possible because of the high selectivity of the indicator electrode to J_3^-/J^- system in comparison with H^+/H_2 system (molecular hydrogen is evolved on cathode during generation of the standard addition of iodine). These redox analysers have been successfully used for more than 3 years at water-supply stations of St.-Petersburg for the potable water chlorination process.

Reference

[1] Pisarevsky A.M., Kaverin A.V. // Rus. J. Appl. Chem, 1999, v.72, №10, pp. 1658-1662.

POTENTIOMETRIC DETERMINATION OF SELENIUM (IV) AND TELLURIUM (IV) BY SULFUR-CONTAINING DERIVATIVES OF PYRAZOLONE

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Sulfur-containing derivatives of pyrazolone - thiopyrine (TP), dithiopyrilmethane (DTM) and its homologues methyl and propyldithiopyrilmethane (MDTM and PDTM) are used for extraction separation of soft cations and their extractive photometric determination. The interaction of listed reagents with selenium (IV) and tellurium (IV) have been investigated in an attempt to use them in potentiometric titration. Dithiopyrilmethane has dissolved in 10M, and MDTA, PDTM in 5M sulfur acid for receiving of reactive forms. Water solution of thiopyrine with concentration 0.0510 mol/L have been used. We have found the correlation between a value of titration jump and carbon chain length, between a value of titration jump and stability constant of forming compounds. Potentiometric method of the determination of selenium (IV) and tellurium (IV) is founded on forming soluble and unsoluble colored compounds. The dependence of potentials of Ag, Au, Pt, Pd, W, Cu and C electrodes from Se(IV) and Te (IV) ions and the listed reagents concentration have been investigated. The highest jump appears on using Ag electrode. Silver chloride reference electrode was used. Silver indicator electrode forms electrochemical system $Mn^{+}/[MRn]$, $[AgR]$, Ag before an equivalence point (eq.p.) acts as the III kind electrode, and acts as II kind electrode after eq.p. forming $R/[AgR]$, Ag system. Optimal conditions of Se(IV) and Te (IV) potentiometric titration have been determined. The acidity intervals created by sulfur acid and sodium hydroxide are equal respectively 0.5-2.4; 1.2-3.5 mol/L (for TP titration), 0.1-4.5; 0.8-3.8 mol/L (for DTM titration), 0.02-2.1; 0.01-3.3 mol/L (for MDTM titration), 0.02-2.9; 0.06-3.6 mol/L (for PDTM titration). As is evident from the foregoing, the acidity intervals increase with lengthening radical. Determined concentration intervals are equal respectively: $(10.5-2.6) \times 10^{-5}$, $(0.3-5.0) \times 10^{-5}$ mol/L for TP, $(0.2-0.5) \times 10^{-5}$; $(1.15-4.70) \times 10^{-5}$ mol/L for DTM, $(1.49-3.0) \times 10^{-5}$, $(0.4-2.0) \times 10^{-5}$ mol/L for MDTM, $(0.7-7.9) \times 10^{-5}$, $(0.7-4.9) \times 10^{-5}$ mol/L for PDTM. Compositions of complexes are Se (IV) : TP=1:3; Se (IV):MDTM (PDTM)=1:4, Te (IV):TP (MDTM, PDTM)=1:4. The procedures are characterized by reasonable selectivity and accuracy.

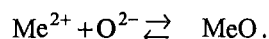
POTENTIOMETRIC STUDIES OF CATION – OXIDE ION INTERACTIONS IN CHLORIDE MELTS OF DIFFERENT ACIDITIES

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Interactions of admixture metal cations with oxide ions may be conditionally divided into strong and weak. In the first case the fixation of oxide ions by excess of cations is practically complete and the interaction can be easily detected by potentiometric titration. Such an interaction is hardly detected in the second case since the fixation of O^{2-} is essentially incomplete and corresponding potentiometric curves are not informative. The second question is connected with the form of the metal-oxide complex – is this non-dissociated oxide in the solution or precipitate? Importance of a routine allowing to solve these problems increases in the case of acidic melts, containing LiCl or alkaline earth halides [1].

Since the routine described in [2] is unavailable for systems with the weak interactions we proposed and confirmed by calculations plotting the obtained data as $E - \log m_{O^{2-}}^0$ graph for reactions



The treatment of mass action law equations for non-saturated and saturated solutions allowed to obtain some sequences, connected with slopes $\partial E / \partial (-\log m_{O^{2-}}^0)$. The plots referred to cases of complete levelling the cation acidity by ionic melt (Cd^{2+} and Pb^{2+} in KCl-LiCl, 700°C), incomplete dissociation of soluble oxide (Pb^{2+}/PbO in $SrCl_2$ -KCl-NaCl, 700°C) and limitation of O^{2-} concentration in ionic melts ($CaCl_2$ -KCl, 700°C) are considered.

References

- [1] V.L. Cherginets and T.P. Rebrova, *Electrochim.Acta.*45(1999)469.
- [2] T.P.Boyarchuk, E.G.Khailova and V.L. Cherginets, *Electrochim.Acta.*38(1993)1481.

SOLID-STATE POTENTIOMETRIC SENSORS FOR THE DISTINCT DETERMINATION OF DIFFERENT TYPE SYNTHETIC SURFACTANTS

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The membrane electrode active compound (EAC) compositions of solid-state potentiometric sensors selective to different type of synthetic surfactants are proposed. EAC are the ionic associates: cetylpyridinium-dodecylsulfate (CP-DDC) and cetylpyridinium-tetraphenylborate (CP-TPB). Inert electron conductors are silver and graphite. The stoichiometric composition, solubility products (SP), thermal stability of the EAC are evaluated. Stoichiometric ratio is 1:1, SP equals $2 \cdot 10^{-11}$ (CP-DDC), $2,3 \cdot 10^{-12}$ (CP-TPB); dissociation constant - $2,8 \cdot 10^{-5}$.

The main electroanalytical characteristics of surfactant sensors are established. Function $E=f(-\lg C)$ linearity range extending from $1 \cdot 10^{-6}$ - $1 \cdot 10^{-2}$ M DDCNa (graphite) and $1 \cdot 10^{-5}$ - $1 \cdot 10^{-2}$ M (silver) for electrodes based on CP-DDS; $\alpha=58 \pm 2$ mV/pC. The exploitation period of sensors with graphite current conductor is 10–12 months, with silver ones – 2–3 months. Considerable exploitation time for electrodes with graphite current conductor is probably connect both with graphite structure and possibility of penetration membrane solvent in it. The dibutylphthalate (DBP) penetration in graphite lattice structure is proved by IR-spectroscopic method. The DBP penetration into graphite requires much time (~24 hours).

The main charge carriers in the investigated systems are DDC⁻, CP⁺ and TPB⁻ ions. These results based on total data, which have been established by means of the methods of conductivity, EMF and applied potential. The electrodes based on CP-DDC have anionic and cationic response – cetylpyridinium, cetyltrimethylammonium – $1 \cdot 10^{-6}$ - $1 \cdot 10^{-3}$ M; $\alpha=56 \pm 2$ mV/pC. The possibility of electrode based on CP-TPB to show the sensitivity in regard to ions CP⁺ ($\alpha=47 \pm 1$ mV/pC) and TPB⁻ ($\alpha=72 \pm 1$ mV/pC) in $1 \cdot 10^{-6}$ - $1 \cdot 10^{-3}$ M range, lets us to recommend studied ionic associate as membrane active compound surfactant-electrodes for the precipitate potentiometric titration of cationic, anionic and nonionic surfactants.

The techniques of potentiometric determination of nonionic surfactants in sewages, cationic surfactants in balsams, distinct nonionic and anionic surfactants determination in shampoos, detergents have been elaborated.

PVC "BLANK" MEMBRANES FOR CHEMICAL SENSOR ARRAYS OF "ELECTRONIC TONGUE"

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The present work deals with the study of electrochemical properties of PVC chemical sensors with "blank" membranes based on PVC with different plasticizers and application of these for multicomponent analysis using "electronic tongue".

The membranes of this type exhibit low selectivity and therefore are hardly practically applicable as discrete selective sensors. However, their enhanced cross-sensitivity to different species in solutions could be of advantage for application in the framework of the sensor array approach.

PVC- based sensors with different ionophores have been suggested for the determination of alkali, alkali-earth and heavy metal ions in different solutions and biological liquids [1]. The aim of the present work was to evaluate the selectivity of "blank" membranes and to compare it with cross-sensitivity factors [2] to choose sensors valuable for a multisensor array of an "electronic tongue".

Selectivity and cross-sensitivity parameters of PVC based membranes with 7 different plasticizers have been estimated, the content of plasticizer in the membrane changing from 25 up to 75 % wt. Sensitivity to ammonium, alkali metal-, alkali earth metal-, heavy metal-cations as well as to Cl^- , NO_3^- , NO_2^- , SO_4^{2-} , CO_3^{2-} anions in individual solutions has been observed.

According to the calculated selectivity values and cross-sensitivity parameters the "blank" membranes were divided into three groups with respect to their possible applicability for multisensor array applications. A good correlation between selectivity and cross-sensitivity for the "blank" membranes has been obtained. The highest cross-sensitivity and, thus, the best perspective for multisensor array of an "electronic tongue" was observed for the membranes containing dioctylphthalate and trihexylphosphate as plasticizers.

References

- [1] A. Legin, A. Smirnova, A. Rudnitskaya, L. Lvova, E. Suglobova, Yu. Vlasov, *Analytica Chimica Acta*, 1999 (385) 131-135.
- [2] Yu. Vlasov, A. Legin, A. Rudnitskaya, *Sensors and Actuators B.*, 1997 (44) 532-537.

POTENTIOMETRIC DETERMINATION OF SOME SULFIDE FORMING METALS IONS BY ANTIPYRILDITHIOOXAMIDE

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Antipyrine and its derivatives as well as their sulfur containing analogs are commonly used for extractive separation and extractive photometric, atomic absorption determination of soft cations. Investigation with the aim of using pyrazolone sulfur containing derivatives in potentiometric titration demonstrated their low selectivity. New reagent antipyrildithiooxamide has been synthesized with the goal of the increase of this compounds class selectivity and their application in titrimetric methods of analysis. For identification of the synthesized compound its molecular mass has been determined by cryoscopy. $M.r.exp.$ 306.58; $M.r.theor.$ 306.43. 0.1M alkali solution of antipyrildithiooxamide has been used for the investigation of this compound interaction with sulfide forming metals ions. Alkali concentration has major influence on the reagent solution stability in time and on a potential difference value of an indicator electrode. Potentiometric method of determination of investigated by us elements is founded on the formation of difficulty soluble colored compounds with the reagent. The dependence of different indicator electrodes potentials (from Ag, Au, Pt, W, Pd, Cu, Sb) on concentration of sulfide forming ions and the reagent (concentration interval $1 \times 10^{-5} - 1 \times 10^{-4}$ M) have been investigated. It has been found that the greatest potential difference was detected on electrodes from Ag, Pt, Au and Pd. The following investigations have been carried out with the indicator electrode made of silver and chlorinsilver reference electrode. The indicator electrode acts as III kind electrode before an equivalence point, electrochemical system $Mn^{+}/[MRn], [AgR], Ag$. After the equivalence point the indicator electrode acts as II kind electrode, forming system $R/AgR, Ag$. Optimal conditions of Ag^{+} , Pd^{+} , Cu^{2+} , Sb^{3+} ions potentiometric titration have been determined. Acidity intervals created by sulphuric acid or sodium hydroxide are 2.0×10^{-3} -3.3; 4.0×10^{-3} -3.3; 8.0×10^{-3} -2.3; 9.0×10^{-2} -3.5 mol/l respectively. Determined concentrations are $(1.5-14.5) \times 10^{-5}$; $(0.6-2.6) \times 10^{-3}$; $(2.2-12.1) \times 10^{-5}$; $(0.4-3.4) \times 10^{-5}$ M respectively. The procedures are distinguished for its quickness, selectivity and have been sampled on silver-palladium and copper-silver alloys.

FORECASTING OF MEMBRANE SELECTIVE PROPERTIES USING CHEMICAL AND ELECTROCHEMICAL PARAMETERS

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Electrode, dynamic, transport and analytical properties of membranes based on metal - polietixylate cationic complexes and organic ion-exchangers are investigated. The proposed electrodes give the response on charged (ionic surfactants, physiologically active amines, penicillin antibiotics) and neutral (nonionic surfactants, phenols) particles.

The state of membrane active components in aqueous and organic media is investigated; the quantitative estimation of their physicochemical characteristics (composition, solubility, SP, stability, dissociation degree) is carried out. The influence of electrode-active materials physicochemical properties on electroanalytical, transport, dynamic characteristics of membranes in solutions of various organic compounds is established. It has allowed to predict the selective properties of electrodes.

The basic stages of potential formation process of selective electrodes based on complex cations and organic ion-exchangers are determined. The basic charge carriers on membrane – solution phase border and in the membrane phase are determined.

It is established, that the arising of membrane potential of electrodes based on metal-polyetoxylate-tetraphenilborate is connected both with the formation of complex cation metal - polyetoxylate and its extraction in membrane phase. The investigation of membrane transport has shown that the complex cations realise the main role in the charge transfer.

On the example of ionic associates the medicine drug – tetraphenilborate, the interrelation between extraction ability of physiologically active amines in dibutylphthalate (dimedrol ~ papaverine > novocaine ~ lidokain) and selectivity of membranes on their basis is determined.

The proposed methodological approach to forecasting of membrane selective properties using EAC chemical and electrochemical parameters is applied to creation of electrodes with optimal analytical parameters selective to cationic, anionic, nonionic surfactants, phenols, physiologically active amines and some antibiotics.

CAPRIC ACID AS A NEW IONOPHORE FOR A LEAD (II) ION-SELECTIVE MEMBRANE ELECTRODE SENSOR

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Heavy metals such as lead, mercury, and cadmium are toxic when absorbed in the body. Their accumulative behavior causes poisoning, cancer, brain damage, and etc. [1]. Because of the increased industrial use of lead, on one hand, and its serious hazardous effect to human health, on the other hand, the electrochemical properties and preparation of the lead ion-selective membrane electrodes have been extensively studied by using different active materials [2].

In this work we employed capric acid [$\text{CH}_3(\text{CH}_2)_8\text{COOH}$] as a suitable ionophore to construct a PVC-based membrane electrode which shows significantly high selectivity to lead ion over alkali, alkaline earth and several transition metal ions. The optimum composition of the membrane was 30wt% poly(vinyl chloride), 60wt% Elvaloy 742 as plasticizer, 5wt% ionophore, and 5wt% potassium tetrakis (p-chlorophenyl) borate as lipophilic salt. The electrode exhibits a Nernstian slope of 30 mV/decade for Pb^{2+} over a wide concentration range (1.0×10^{-5} - 1.0×10^{-2}). The proposed electrode revealed good selectivities for Pb^{2+} over a wide variety of other metal ions and could be used in the pH range of 4-7. It shows a good stability, good reproducibility, wide range of pH independency, and fast response. The electrode was used for the potentiometric titration of chromate ions with lead ions.

References

- [1] B. Volesky, "Removal of Heavy Metals by Biosorption", in Biosorption of Heavy Metals (B. Volesky, Ed.), CRC Press, BocaRaton, FL, 1990.
- [2] M. F. Mousavi, N. Alizadeh, M. Shamsipur and N. Zohari, Sens. Actuators B, (2000) in press.

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PHYSICOCHEMICAL CHARACTERISTICS OF COMPOUNDS METAL-POLYETOXYLATE-TETRAPHENILBORATE: ELECTROANALYTICAL AND TRANSPORT PROPERTIES OF MEMBRANES BASED ON

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The state of metal-polyetoxyate-tetraphenilborate (Me-PEO-TPB) electrode-active compounds (EAC) in water, in the medium of solvent-plasticizer and in the membrane phase is investigated. The quantitative estimation of their physicochemical characteristics are carried out. Polyetoxyates were both polyethyleneglycols with various molar weights (PEG-600, -1500, -2000) and nonionic surfactants (NS) – polyetoxyated nonylphenols (NP-m) $C_9H_{19}-C_6H_4-O-(C_2H_4O)_m-H$ ($m = 8, 12, 25, 30, 60, 100$), polyetoxyated alcohol synthanol $C_{17}H_{35}-O-(C_2H_4O)_7-H$, acid stearox-6 $C_{17}H_{35}-COO-(C_2H_4O)_6-H$, amide of acid synthamid-5 $C_{17}H_{35}-CONH-(C_2H_4O)_6-H$; Me – Pb^{2+} , Ba^{2+} , Ca^{2+} . The determining influence of stability, composition, solubility products and EAC dissociation degree both on the electroanalytical and transport characteristics of membranes was shown.

It is shown that the stability of complex cations grows with increase of the etoxyate chain length and hydrophobicity of PEO terminal group in its composition. With the increase of complex cation stability the detection limits both of cations ($\sim 10^{-7}$ mol/l Pb^{2+} and 10^{-5} mol/l Ba^{2+}) and NS (10^{-6} mol/l NP-12 and 10^{-3} mol/l NP-100) decrease. The selectivity rows of electrodes in solutions of NS do not depend from the nature of PEO in the EAC composition. The membranes are more selective to hydrophobic NS: stearox-6 > NP-8 > synthanol-7 > synthamid-5. In solutions of NP proposed electrodes show the larger selectivity to NS with smaller number of etoxyate groups.

The dependence of characteristic temporal parameters of electrodes in NS solutions on membrane and solution composition is obtained. The response time (t_{95}) is influenced by two processes: 1) the formation of complex cations Me-PEO, as τ_1 depends on complex cations stability; 2) transport of complex cations $[Me-PEO]^{2+}$ in the membrane phase, as τ_2 decreases with increase of NS hydrophobicity in its composition. The study of membrane transport has shown, that the contribution of complex cations to charge transfer decreases with increase of the etoxilate chain length in EAC composition.

A STUDY OF THE SENSITIVITY OF CHEMICAL SENSORS TO ORGANIC SUBSTANCES IN SOLUTIONS

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The analysis of liquid media, containing various organic substances, namely different kinds of beverages and foodstuffs is an urgent analytical task. In the recent years a promising approach to these problems based on the utilization of sensor arrays and pattern recognition/multivariate analysis methods ("electronic tongue") has been suggested. To provide meaningful and reliable information about complicated multi component systems such as wines, coffee, beer, milk, etc., the sensors of the array should exhibit reproducible sensitivity to organic substances. On the other hand, the most widespread sensors for "electronic tongue" are potentiometric electrodes, which are not reported to be sensitive to organic species. The aim of the present work is the development of new sensing materials for chemical sensors and evaluation of their sensitivity to various organic substances in model solutions and in different foodstuffs.

Two main types of sensing materials have been studied: solid-state compositions on the basis of multi element chalcogenide glasses and PVC based organic polymer membranes. Attention was paid to non-specific materials with enhanced cross-sensitivity to different species in solutions. Totally, over 100 of different sensors have been prepared and evaluated. Typical organic substances from different classes, usually present in foods, have been tested. They were alcohols, organic acids, phenols, ethers, aldehydes, terpenes and also some typical "basic taste" substances, such as quinine, urea, etc. From 3 to 10 substances of each class have been studied. The concentration ranges were from 10^{-5} mol/L to 10^{-1} mol/L and even higher for selected substances. Different beverages and foodstuffs were analyzed too.

It was found that some sensors, both solid-state and PVC, display reproducible sensitivity to organic compounds from each class studied. The response could be linear, with the slope up to 100 mV/decade and non-linear but still reproducible. A non-linear data can be also useful working with the sensor arrays. The obtained sensors have been incorporated into the array of an "electronic tongue" which was successfully used for quantitative analysis and qualitative recognition of different foodstuffs.

AL-SELECTIVE MEMBRANE ELECTRODE BASED ON FURIL

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Dispite the existence of widespread published papers on the development of ISEs on single-and double-charge cations in the literature [1, 2], much less attention has been paid to the preparation of ISEs for triple-charge cations such as Al(III).

In this work, we use of furil (Ethan dione, di-(2-furyl)) as an good neutral carrier in construction of a Al(III)-PVC membrane electrode. The sensors shows a Nernstain response for Al(III) ions (18.5 mV/decade) over a wide concentration range (1.0×10^{-7} - 1.0×10^{-2}) with a limit of detection 1.0×10^{-7} .

The response time of the sensor is fast and the membrane can be used for more than two months without observing any deviation.

The electrode revealed very good selectivites for Al(III) over a wide varity of other metal ions and could be used in a mild pH range (4.0-7.0). It was used as an indicator electrode in potentiometric titration of Al(III) ions.

References

- [1] L. X. Sun, T. Okada, J. P. Collin, H. Sugihara, Anal. Chim. Acta, 329(1996)57.
- [2] M. F. Mousavi, N. Alizadeh, M. Shamsipur and N. Zohari, Sensors & Actuators B, in press.

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POTENTIOMETRIC MEASUREMENTS WITHOUT REFERENCE ELECTRODE USING A SENSOR SYSTEM OF "ELECTRONIC TONGUE"

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The possibility to make measurements with an array of potentiometric chemical sensors in solutions ("electronic tongue") without a standard reference electrode has been investigated. In many practical applications a conventional way of measurement of sensor potential (e.m.f.) using a reference electrode causes a number of problems, e.g. with miniaturization. A perspective to make potential measurements without any reference is very attractive. In theory, it is possible to avoid using a reference electrode. The measurements may be made vs. one of the sensors of the array and the resulting cross-voltages between the sensors of the array should be considered. If array consists of 3 different sensors, which outputs are not correlated, there will be 3 cross-voltages that will contain the same information as conventionally measured potential values. Bigger number of the sensors in the array will result in a number of redundant cross-voltages. Highly correlated cross-voltages could be rejected.

Evaluation of the sensor array of an "electronic tongue" without a standard reference electrode has been carried out in drinkable mineral waters samples. Real measurements with the sensor array have been made vs. conventional silver/silver chloride reference electrode. Cross-voltages (differences between potentials of different sensors) have been calculated. The values of cross-voltages do not depend on the "physical" presence of a reference electrode. Both types of the data – with and without reference, have been processed using principal component analysis (PCA) and compared to each other.

It was found that in both cases the system ("electronic tongue") is capable to distinguish reliably between all samples and the result of recognition does not depend on the data used. The only difference is the absolute sample positions on the PCA plots, but this does not affect distinguishing ability of the "electronic tongue". Thus, it is possible to use the sensor array of "electronic tongue" without a standard reference electrode, at least in selected cases.

**POTENTIOMETRIC PROPERTIES OF ANION-SELECTIVE PVC MEMBRANES
CONTAINING TWO ION-EXCHANGERS WITH OPPOSITELY CHARGED
SITES.**

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Remarkable effect of simultaneous existence in membrane phase of both anionic and cationic sites taken in optimal molar ratio is observed. This effect is shown for membranes based on different quaternary ammonium salts and potassium tetrakis (4-chlorophenyl) borate as cation-exchanger. Besides this the effect is demonstrated for neutral-carrier based membranes containing two ion-exchangers with opposite charges of lipophilic groups.

It was shown that substitution of potassium tetrakis (4-chlorophenyl) borate by its more lipophilic derivative tetrakis [3,5-bis (trifluoromethyl)phenyl]borate increase the membrane selectivity towards basic anions in comparison to lipophilic ones.

Based on these results the highest so far reported selectivity to carbonate anions in comparison to all tested interfering anions have been realized for the membranes containing quaternary ammonium salt together with potassium and hexyl p-trifluoroacetylbenzoate as neutral carrier.

The origin of the effect was studied using impedance spectroscopy. The found relationship between the apparent exchange current densities and bulk resistance for membranes containing cation-exchanger and without it supports the assumption that the selectivity determines especially by the processes at the membrane solution boundary.

The influence of QAS structure on the bulk and charge transfer resistances was studied using impedance spectroscopy. It is shown that only membranes with more lipophilic QAS have low charge transfer resistances after 3 weeks of soaking what is corresponding to a Nernstian carbonate response for those membranes.

ISFET BASED BIOSENSOR FOR TRIACYLGLICERIDES

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In human organism lipids are presented in a reserved form of triacylglycerids (TAG). Their content in blood depends on the state of an organism. Determination of the TAG concentration is very important for the clinical diagnostics and for the control of the quality of medicines and foods. As a rule, this procedure is fulfilled by routine biochemical methods that are time consuming and demanding sparse chemicals as well as work of high professionals. Taking into account the role of the TAG in living organisms, large attention is paid for the improvement of the existing methods and development of new effective approaches to record the content of these substances. In this respect enzymatic sensors may provide the best fulfilment of practical demands. Unfortunately, working with these substances, in order to create a sensor with subsequent successful application, one encounters a number of difficulties. Probably this is the reason for scanty publications in this area.

In this report we present experimental results about possibility to develop an enzymatic sensor based on lipase as a sensitive element and ion-selective field effect transistors (ISFETs) as a transducer for the determination of the TAG in a solution.

As a result of our investigations, ISFETs based lipase sensor was created. It allows determining TAG concentrations in a solution in the range of concentrations from 0.1 to 2 mmol/l. The sensitivity of this enzymatic sensor is about 0.1 mmol/l. The analysis is complete in about 2 min. The curve, that presents sensor signal as a function of the substrate concentration, achieves plato at 4 mmol/l of the trioleine content in solution. The sensor response to trioleine in the concentrations equal to 1, 2, and 4 mmol/l was 192, 270 and 290 mV respectively. The optimal condition for the enzymatic reaction and its recording was provided by the use of 1 mmol/l sodium phosphate buffer solution, pH 7.3.

It was concluded that the developed model of lipase sensor based on the ISFET is challenging for practical application at the control of the TAG level in real samples.

PB(II)-SELECTIVE MEMBRANE ELECTRODE BASED ON RECENTLY SYNTHESIZED 1,4-BIS(PROPO-2-ENYLOXY)-9,10-ANTHRAQUINONE

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Lead poisoning is one of the most common problems in most large cities. Lead is especially harmful to children younger than 6, but anyone who eats, drinks or breathes something which has too much lead can get lead poisoning.

Large amounts of lead in a child's blood can cause brain damage, mental retardation, behavior problems, anemia, liver and kidney damage, hearing loss, hyperactivity, developmental delays, other physical and mental problems, and in extreme cases, death [1].

In this work we employed a recently synthesized derivative of anthraquinone 1,4-bis(propo-2-enyloxy)-9,10-anthraquinone as a suitable ionophore to construct a PVC-based membrane electrode which shows significantly high selectivity to lead ion. The sensor shows a Nernstian response for Pb²⁺ ions over a wide concentration range (2.5×10^{-6} - 1.0×10^{-2}). The response time of the sensor is fast (15 s) and the membrane can be used for more than three months without observing any deviation. The electrode revealed comparatively excellent selectivities with respect to alkali, alkali earth and some transition metal ions. It shows a good stability, good reproducibility, and fast response. The electrode was used for the potentiometric titration of Pb (II) ion.

References

- [1] B. Volesky, "Removal of Heavy Metals by Biosorption", in Biosorption of Heavy Metals (B. Volesky, Ed.), CRC Press, BocaRaton, FL, 1990.

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SAPPHYRIN – BASED ION-SELECTIVE ELECTRODES FOR RECOGNITION OF DICARBOXYLATE ANIONS

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This abstract deals with the problem of dicarboxylate recognition and ion-selective electrodes (ISEs). The family of sapphyrin dimers, bearing various bisamide spacers was shown to display excellent recognition properties for dicarboxylate anions [1]. Taken into account this fact the generation of open-chain **1-2** and cyclic **3** sapphyrin dimer systems (containing (1*S*,2*S*)-1,2-diamino-cyclohexane (**1**, **3**) and (*S*)-2,2'-diamino-1,1'-binaphthalene (**2**) spacers) served as the binding subunits into poly(vinyl chloride) (PVC)-membrane ISEs. Herein, the potentiometric selectivity of investigated receptors was determined toward the linear homologues, positional, geometrical and optical isomers of dicarboxylate substrates.

The experimental data obtained indicate that (i) in contrary to open-chain **1**, the cyclic sapphyrin dimer **3** displays a preference for aliphatic over aromatic substrates; (ii) enantioselectivity of the diaminocyclohexane-derived dimers **1** and **3** to glutamate is higher than of the binaphthalene-containing receptor **2** ($K_{(+)} / K_{(-)} = 7.28, 2.59$ and 0.45 , respectively); (iii) the enantioselectivity of both open-chain and cyclic dimers to N-Cbz-aspartate controls by the plasticizer polarity.

Reference

[1] Sessler, J.L.; Andrievsky, A.; Král, V.; Lynch, V. J. *Am. Chem. Soc.* **1997**, *119*, 9385 – 9392.

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DRUG INVESTIGATION BY THE MONOAMINE OXIDASE BIOSENSOR

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Potentiometric biosensor on the base of immobilized rat liver monoamine oxidase (MAO) for substrates determination have been designed in our previous paper [1].

In the present research this biosensor was used for the investigation of some drugs - MAO inhibitors : aceclidinum, methacinum, sibazonum, atropinum, scopolaminum (reversible MAO inhibitors) and tacrine, proflavinum and tryptaflavinum (irreversible MAO inhibitors). Gas-gap sensor on the base of glass disc pH-metric electrode (St.Peterburg University) was used as the analytical detector. Isolated during desamination of MAO substrates (serotonine, tyramine, benzylamine) ammonia change the analytical detector potential. This changes became lower in the drug presence. The size of this change depends on the drug nature and concentration.

The calibration curves $E=f(-\lg[I])$, i.e. potential dependence against the inhibitor concentration, at the certain substrate concentration and certain preincubation time (for irreversible inhibitors) was plotted. It was shown, that selectivity, the measurable concentration range and the limit of drug detection depend on the nature and concentration of MAO substrate. The detection limit for aceclidinum was $1.5 \cdot 10^{-6}$ M (substrate - serotonine), $4 \cdot 10^{-5}$ M (tyramine) and $5 \cdot 10^{-3}$ M (benzylamine), for tacrine it was $3 \cdot 10^{-9}$ M (serotonine), $5 \cdot 10^{-9}$ M (tyramine) and $2 \cdot 10^{-8}$ M (benzylamine) when 45 min preincubation.

Reference

- [1] O.V. Yagodina and E.B. Nikolskaya. Sensors and Actuators B, 1997, 44, 566.

DODECYL BENZENE SULFONATE ION-SELECTIVE ELECTRODE BASED ON POLYANILINE-COATED PLATINUM MODIFIED ELECTRODE

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Because of the widespread use of conducting polymers in different areas, such as rechargeable batteries[1] and chemically modified electrodes[2,3], the construction of new polymer based sensors are increasing interest. A proper polymer film directly coated on the electrode surface improves the quality of the electrode surface. Based on the doping and dedoping processes, structure, conductivity and electrochemical properties of these conductive polymers, they can be modified and used as a device for determination of chemical species.

In this work we report a new method for the determination of dodecyl benzene sulfonate(DBS) by using polyaniline as conductive polymer for the modification of a Pt electrode. The polyaniline coated Pt electrode was prepared electrochemically in the solution containing 0.001 M aniline and 0.007 M DBS. The potentiometric response of the prepared electrode under different experimental conditions was optimized and the polymeric film prepared by passing $7.5 \text{ coulomb.cm}^{-2}$ electricity showed the best response. The electrode exhibited a good Nernstian slope of $59.1 \pm 0.3 \text{ mV.dec}^{-1}$ for DBS ion over a wide concentration range ($5.0 \times 10^{-6} - 1.0 \times 10^{-2}$). The proposed electrode revealed good sensitivities for DBS ion over a wide variety of other anions and can be used in the wide pH range of 4-12. It showed a low detection limit ($5 \times 10^{-6} \text{ M}$), good stability, good reproducibility and fast response (response time < 20 seconds). The proposed electrode was used for the determination of DBS in real samples.

References

- [1] M. Nishizawa And I. Uchida, *Electrochimica Acta*, 44 (1999) 3629-3637
- [2] T. Lindfors, J. Bobacka, A. Lewenstam and A. Ivaska, *Electrochimica Acta*, 43 (1998) 3503-3509
- [3] S. Shahrokhian, M. K. Amini, S. kolagar, S. Tangestaninejad, *Microchemical Journal*, 63 (1999) 302-310

ELECTROCHEMICAL CONTROL OF PESTICIDE LEVEL BY IMMUNE SENSOR BASED ON THE ISFET

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Nowadays different types of biosensors are developed for the analysis of pesticides in solution. In this report we present experimental results about use of the ISFET as a transducer for the creation of an immune sensor to determine simazine and 2,4-D. In order to monitor these pesticides polyclonal antibodies were obtained. We utilised two ways of attaching antibodies to the ISFET gate: (1) via glutaraldehyde and the protein A; (2) via polyelectrolyte self-assembly (polyalylamine hydrochloride and polystyrenesulfonate sodium salt) and the protein A. The immune analyses were carried out in a competitive way. In this case the native and labelled by horseradish peroxidase pesticides competed for binding sites on the immobilised antibodies. The activity of horseradish peroxidase was determined in the presence of the substrate and ascorbic acid. The concentration of hydrogen peroxide added to the measuring cell was chosen experimentally and it was equal to 5 and 10 mM.

It was shown that in case of antibody immobilisation via glutaraldehyde and the protein A the sensitivity limit for these antigens was 1.25 ng/ml with the sensor response linear in the range 5-175 ng/ml. The immune sensors with antibodies immobilized via polyelectrolytes and the protein A showed higher sensitivity (almost one order). The last method turned out to be the most efficient for the immobilisation of the immune components on the ISFET surface. The analysis has rapid kinetics of reaction, being complete in 40-50 min. In the case of use of special immune chemical approach ("saturation" of binding sites, remained after interaction with free pesticide, with simazine labelled by horseradish peroxidase) the sensitivity of the analysis was 5 times higher. After the treatment of the chip with a solution with low pH, the ISFET with antibodies on the surface was used as longest 2-3 times with good reproducibility of the results. The possibilities to improve the sensitivity of the analysis and perspective of its practical use are discussed as well.

NEW POTENTIOMETRIC BIOSENSORS FOR AMINE DETERMINATION

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The potentiometric properties of biosensors for monoamine determination utilizing monoamine oxidase from pig and rat liver, has been reported in a previous paper [1].

In the present research the influence of the biomaterial nature on the amine biosensor selectivity and the defined amines assortment have been studied. Several potentiometric biosensors on the base of amine oxidases (AO) from squid *Todarodos Pacificus* liver, infuzoria *Tetraphymena puriformis* and bacteria *Methanosarcina barkeri* have been designed. AO were partly purified by the extraction in the potassium-phosphate buffer. These preparations were immobilized in gelatin and agar by glutaric aldehyde treatment of enzyme-containing gel and by mechanic claw in cellophane cells. In the composition of biosensors two types of analytical detectors have been used: pH-metric polyvinyl chloride solid state electrode (St. Petersburg University) and gas-gap sensor on the base of glass disc pH-metric solid state electrode [2].

Functional details (response range, response time, sensitivity, stability, etc.) of new amine biosensors have been investigated. The optimal conditions of amine determination by these biosensors were studied.

The working out AO-biosensors allow to determine microconcentrations of some amines - AO substrates: tyramine, serotonin, benzylamine, hystamine and adrenaline. The obtained results permitted us to work out the special methods both of the amine sum detection and individual amines detection in the time of common presentation in the sample.

References

- [1] O.V. Yagodina and E.B. Nikolskaya. Sensors and Actuators B, 1997, 44, 566.
- [2] O.V. Yagodina and E.B. Nikolskaya. Analytica Chimica Acta, 1999, 385, 137

Poster Contributions

Session B

IN SITU ANALYSIS OF CATIONIC SURFACTANTS ON SILVER ELECTRODE SURFACES BY SERS MICROPROBE SPECTROSCOPY

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Surface-enhanced Raman microprobe spectroscopy (micro-SERS)¹ has been used to study, in situ, the adsorption process of cetylpyridinium bromide (CPB), cetyltrimethylammonium bromide (CTAB) and their binary mixtures adsorbed on charged silver surfaces. Micro-SERS spectroscopy permits the acquisition of surface Raman spectra from electrode spots down to 1 μm in size or other forms to microsamples approaching the subpicogram level.

The spectra are compared both to the normal Raman spectra of the corresponding solid and solution species and to the ab initio calculated Raman spectra (HF, DFT) in the quantum-mechanical oligomer approach. Examining the frequency shifts and the changes in relative intensities of the CPB bands due to adsorption and to potential variation reveals an enormous enhancement for the in-plane ring vibrations of the head-group (ring breathing vibration $\nu_1(A_1)$ and ring stretching vibration $\nu_{8a}(A_1)$) while the bands assigned to vibrations of the $(\text{CH}_2)_n$ alkane chain (symmetric and antisymmetric C-C vibrations, $(\text{CH}_2)_n$ scissor and $(\text{CH}_2)_n$ torsion vibrations, and symmetric and antisymmetric CH_2 stretch vibrations) are nearly absent. These results suggest that the pyridinium ring is adsorbed perpendicularly with respect to the silver surface and that the hydrocarbon chain is directed away from surface. In contrast, the CTAB surfactant is adsorbed with the head-group pointing to the surface and the hydrocarbon chain is adsorbed flat with the tail running parallel to the surface.

Coadsorbed halide ions are very important for the binding mechanism in the first monolayer. The positively charged head-groups are surrounded by bromide ions and the pyridinium/bromide and trimethylammonium/bromide surface-complexes are strongly adsorbed even on positively charged surfaces.

Competitive coadsorption measurements of the binary surfactant mixtures have shown that the adsorption process at the solid/liquid interface depends greatly on the surface charge and the relative concentration of the CPB/CTAB mixture. A fully equilibrated monolayer coverage of the same amount of CPB and CTAB is observed from a bulk surfactant mixture concentration ratio of CPB:CTAB=1:1000. The adsorption geometry of CPB in this mixed monolayer of CPB and CTAB (patchy hemimicelles of CPB and CTAB) is strongly influenced by the surface charge.

In addition it is shown that the use of electrode micro-SERS spectroscopy is a sensitive analytical technique for trace analysis² by detecting CPB and CTAB on a dried electrode surface in the sub-nanogram range and a powerful tool for characterizing self-assembled monolayers (SAMs). In order to reveal the optimal conditions for this kind of surface-enhanced Raman scattering spectroscopy, atomic force microscopy (AFM) was applied to investigate the surface morphology of silver electrodes exposed to different charge transfer values.

References

1. E. Koglin, S. Kreisig, T. Copitzky; "Adsorption of organic molecules on metal nanostructures: state of the art in SERS spectroscopy", *Prog. Colloid Polym. Sci.* 109(1998)232-243
2. S. Kreisig, E. Koglin, M. J. Schwuger; *Langmuir*, 12(1996)5279-5288

MICROSCOPIC IMMUNOMAGNETIC BEAD DOMAINS AND DETECTION BY SCANNING ELECTROCHEMICAL MICROSCOPY IN ELECTROCHEMICAL IMMUNOASSAY

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A novel procedure to deposit biochemically active microscopic domains of paramagnetic beads is described. The deposition involves applying a magnetic field on a hanging droplet of bead suspension to pull the beads to the bottom of the droplet before printing the beads on a hydrophobic surface (Fig. 1). Scanning electron micrographs showed well-defined and mound-shaped structures whose shape and size depended on the number of beads in the droplet (Fig. 2). The feasibility of using such microstructures in a miniaturized heterogeneous immunoassay is tested by making bead structures with samples from a sandwich immunoassays done in test tubes. The model analyte mouse-IgG is used with alkaline phosphatase (ALP)-labeled secondary antibody (Ab*) in the immunoassay. 4-Aminophenyl phosphate (PAPP) is chosen for the ALP substrate and the enzymatic product 4-aminophenol is detected with scanning electrochemical microscopy (SECM) in the generation-collection mode. Working with bead mounds that had a top-view radius of 125 μm , a detection limit of 1.5×10^{-15} moles of mouse-IgG is obtained.

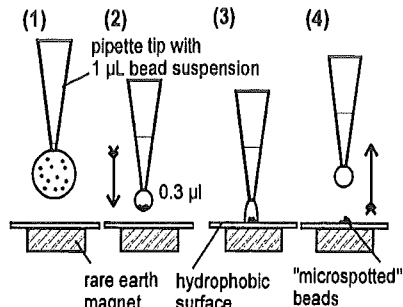


Fig.1

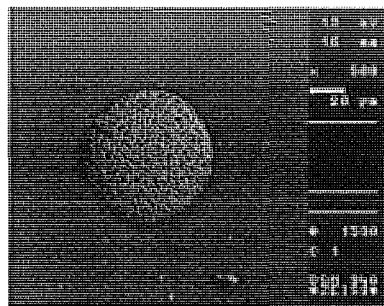


Fig. 2

ON THE DETERMINATION OF STANDARD RATE CONSTANTS USING ULTRA-MICROELECTRODE ARRAYS AND ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY AT LOW FREQUENCIES

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The mass transport controlled AC behaviour of microdisc electrodes has been previously described [1]. General expressions had been derived for the real and imaginary parts of the impedance that could be solved numerically. According to this work, the low frequency branch of the Bode plot became a semicircle, and it could be shown that the deviation from ideal Warburg behaviour is due to the spherical diffusion occurring at microelectrodes.

Here we report on the possibility to use electrochemical impedance spectroscopy (EIS) in the low-frequency range as a novel method for determination of k^0 . The measurements have been performed using either $[\text{Fe}(\text{CN})_6]^{4-/3-}$ or $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ and a single-chip potentiostat developed previously at the IMS [2]. The Bode plot of an EIS experiment at a 3x3 ultramicro electrode array (UMA) with 5 μm electrode diameter shows two semicircles. The semicircle at high frequencies is associated with the charge transfer resistance R_{ct} from which k^0 can be calculated.

However, with decreasing microelectrode radius a_0 the measuring system has to be extremely accurate due to the observed high impedances and high frequencies. Thus, large errors might be expected for the obtained k^0 -values. However, by using an UMA the impedance is significantly reduced due to the parallel connected microelectrodes. Additionally, we could demonstrate, that the distance Δ_k needed to shift the low frequency circle on the real axis until it matches with the theoretically derived curve is inverse proportional to k^0 . The values calculated for k^0 match in this way very well to related literature values. We conclude that EIS at very low frequencies in combination with UMA provide an easy and powerful tool for deriving standard rate constants even of very fast charge-transfer reactions.

References

- [1] M. Fleischmann, S. Pons: „The Behavior of microdisk and microring electrodes. Mass Transport to the disk in the unsteady state - the ac response“, Journal of Electroanalytical Chemistry, 250, 1988, pp. 277-283
- [2] O. Köster et al.: „Single-Chip CMOS Potentiostat für amperometrische chemische Sensoren“, ITG-Fachbericht Nr. 148: Sensoren und Meßtechnik - Fachtagung der Informationstechnischen Gesellschaft im VDE, VDE-Verlag Berlin, 1998, pp. 93-97

**INDIVIDUALLY ADDRESSABLE GEL-INTEGRATED MICROELECTRODE
ARRAYS FOR HIGH RESOLUTION OF THE TRACE METAL
CONCENTRATION PROFILE MEASUREMENTS AT LIQUID-LIQUID AND
LIQUID-SOLID INTERFACES**

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The biophysiochemical processes that influence the circulation of trace metals in natural aquatic system are still ill-known due to their complexity. The highly variable nature of their supply, mixing and removal processes in lakes and oceans results in a great diversity of metal distribution in water column and sediments. Knowledge of their concentration profile at the sediment-water interface is essential to understand chemical and biological processes in sediment. They are also required to understand the dynamic mechanisms of remobilization, solubility, and sorption, and the exchange fluxes of solutes between sediment and the overlying water. Since the thickness of chemical strata of sediment may be as low as a few millimeters, measurements with high spatial resolution are an analytical prerequisite to model diagenetic processes, calculate fluxes of nutrients and electron acceptors through the boundary layer and enable a clear understanding the biogeochemical processes at sediment-solution interface.

We have developed a novel voltammetric probe, which consists of a gel-integrated, Hg-plated, Ir-based microelectrode arrays with 64 individually addressable lines, a powerful double multiplexing system and a single potentiostat. This is the first reported system which allows simultaneous recording of 64 complete voltammograms with fast dynamic techniques such as square wave voltammetry. The capability of this system for real-time, high spatial resolution concentration profile measurements have been tested at well-controlled liquid-liquid and solid-liquid interfaces with steep concentration gradients. The liquid-liquid interface was formed by two layers of aqueous solutions with different components; only one layer contained trace metal ions (Pb(II) and Cd(II)). The individually addressable microelectrode arrays was placed at the interface of the liquid-liquid system; the concentration profiles were recorded as function of time and the effective diffusion coefficients were calculated. The solid-liquid interface was formed from an aqueous solution layer above a layer of silica particles with pores saturated by an aqueous solution. The novel sensor arrays has been used to monitor the diffusion processes of Tl(I) and Pb(II) from the water phase to the solid phase. The influences of porosity, geometry of the porous media and complexation between Pb(II) and silica, on the diffusion processes have been studied. All of these results show that this novel microsensor arrays is capable of measuring the correct real-time diffusion profiles of solutes at interfaces with a 200 μm resolution. Our main future objective is the application of this system for in situ profiling at sediment-water interface. However, potential applications are also foreseen in the biological and medical areas.

COUPLED HEAT AND MASS TRANSPORT AT A DIRECTLY AND CONTINUOUSLY HEATED WIRE

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Microelectrode wires heated directly in situ by electric current generate mass as well as heat energy transport phenomena. With continuous heating, a stationary surface temperature is established as a result of thermally promoted convection [1-3]. The geometry of both temperature and concentration profiles, which are investigated by cyclic voltammetry, potential step experiments and finite element simulation of convection and diffusion processes, are well defined and reproducible. The temperature profile expands into solution much further than any concentration profile that could be generated by electrochemical processes. Temperature differences inside any diffusion layer are low. Consequently, electrochemical reactions including transport processes proceed under nearly uniform temperature conditions. At continuously heated electrodes, real values for the diffusion coefficient at electrode surface temperature can be determined. It is shown that the Nernst diffusion layer approaches a constant, temperature independent thickness if the temperature difference between bulk and electrode surface exceeds a certain temperature [4]. The effect of physical properties of different solvents on the diffusion layer thickness is discussed.

References

- [1] P. Gründler, A. Kirbs and T. Zerihun, *Analyst* 121 (1996), 1805
- [2] P. Gründler, *Fresenius J. Anal. Chem.*, 362 (1998), 180
- [3] A. Kirbs, Dissertation Universität Rostock, 1999
- [4] A. Beckmann, B. A. Coles, R. G. Compton, P. Gründler, F. Marken and A. Neudeck, *Journal Physical Chemistry B*, ASAP

DETERMINATION OF DIFFUSION COEFFICIENTS OF ELECTROACTIVE SPECIES BY MEANS OF MICROELECTROCHEMICAL "TIME-OF-FLIGHT" EXPERIMENTS

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Presently, determination of diffusion coefficients of redox-active species can be performed by means of electroanalytical techniques e.g. chronoamperometry, cyclic voltammetry. However, these methods are averaging the diffusion coefficients of all redox compounds in the solution and hence a simultaneous determination of the diffusion coefficients of several redox species with unknown concentrations is not possible.

Here, we present a novel method for the determination of diffusion coefficients of redox species combining the special properties of a nanodispensing device [1] and microelectrodes. The nanodispenser allows to shoot very small drops (down to volumes of 100 pL) with high reproducibility over a distance of about 2 cm. In the proposed "time-of-flight" experiments the time between shooting of a single drop of a solution containing the redox-active compound and the time until a maximum current at a microelectrode is obtained, has to be determined. For this, the microelectrode is positioned in a known distance from the contact point, at which the nano-droplet is shot, and the distance between this spot and the electrode can be varied by means of a micropositioning system. By choosing the appropriate working potential at the microelectrode one is able to distinguish selectively between different redox species in the solution. Moreover, since the diffusion time of the redox species is evaluated, redox compounds which differ significantly in their diffusion coefficients lead to clearly separated current peaks in the obtained current-time plots.

The time of the current peak in the current vs. time plots and the known distance between two dispensing points can be used to estimate the diffusion coefficient of the electroactive species without knowledge of any system parameters like concentration of the redox species, diameter of the electroactive surface or number of transferred electrons.

Reference

[1] P. Önnérfjord, J. Nilsson, L. Wallmann, T. Laurell, G. Marko-Varga: Anal. Chem. 70 (1998) 4755.

SCANNING ELECTROCHEMICAL MICROSCOPY WITH IMPROVED RESOLUTION, CONSTANT-DISTANCE CONTROL AND SURFACE-TILT COMPENSATION

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By means of scanning electrochemical microscopy (SECM) an electrolyte-covered surface can be characterised or modified using a disk-shaped microelectrode which is positioned in close distance to the sample surface. During scanning the microelectrode over the sample the Faraday current is measured which is representative for the local chemical activity. Since this current is a function of both the tip-to-sample distance and the local activity, it is indispensable to control this distance during scanning. This is, as a matter of fact, even more important for smaller electrodes and for the investigation of three-dimensionally surface structures.

Recent attempts have led to the implementation of a shear-force based feedback control, which allows to keep the tip-to-sample distance constant [1]. The microelectrode is oscillating in its resonance frequency, and the phase shift and/or amplitude shift on approaching the surface is kept at a defined value to attain a constant damping of the tip vibration. However, since the damping is transduced by means of a laser beam, difficulties arise with decreasing size of the microelectrodes and due to the necessity to integrate parallel optical windows into the walls of the electrochemical cell. In addition, a tilt between the sample surface and the plane of the electrode disk leads to an increase in the minimum positioning distance and hence to a decrease of the Faraday current and the resolution of the SECM. For application in scanning nearfield optical microscopy (SNOM) a non-optical shear-force detection system has been described recently [2].

Here, we present an optimised SECM set-up with integrated non-optical shear force detection system adapted to the specific needs of the SECM in that respect that the microelectrode exchange is facilitated and different types of microelectrode geometry can be used. Moreover, the surface tilt angle between microelectrode and sample surface can be compensated for by means of micrometer screws. Imaging of microelectrode arrays and micro-biosensor surfaces is used to demonstrate the improved resolution and the quality of the implemented constant-distance control.

References

- [1] Ludwig, M.; Kranz, C.; Schuhmann, W.; Gaub, H. E. *Rev. Sci. Instr.* **1995**, 66, 2857.
- [2] Brunner, R.; Bietsch, A.; Hollricher, O.; Marti, O. *Rev. Sci. Instr.* **1997**, 68, 1769.

AMPEROMETRIC DETERMINATION OF THE TOTAL ACIDITY OF DISTILLED SPIRITS WITH PLATINUM MICROELECTRODES

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The total acid content is a routine analytical parameter for quality control of alcoholic beverages. Classical acid-base titration methods, based on dyes or potentiometry with a glass electrode, are usually employed for the determination of such parameter [1]. These classical approaches, however, are not suitable for on-line measurements during the production. Moreover, in matrices with high alcoholic content, they show low reproducibility and accuracy.

In previous papers [2,3] we have reported on the possibility of monitoring the acid content of aqueous solutions by voltammetry using platinum microelectrodes. This method is based on the reduction of strong and weak acids present in the matrix, *via* the hydrogen evolution process.

In this communication, we present the results of an investigation on the possibility of applying voltammetry or amperometry at platinum microelectrodes for the determination of the total acidity in distillates, with alcoholic content ranging from 38 to 70%. Preliminary, the voltammetric behaviour of acetic acid, which is the prevailing acidic component of the considered media, was investigated in different synthetic hydro-alcoholic mixtures with ethanol content ranging from 30 to 80%(v/v). This study has allowed to establish the validity of analytical expressions relating the steady-state limiting current, I_L , of the reduction process involved and the analytical concentration of the acid, C_{HA} , as well as the detection limits of acetic acid in the different hydro-alcoholic mixtures. The optimised procedure was then transferred to the analysis of several commercial spirits, as whisky, rum, gin, vodka, grappa.

References

1. A. Amerine, H.W. Berg, R.E. Kunkee, C.S. Ough, V.L. Singleton and A.D. Webb, "The Technology of Wine Making", 4th Ed., AVI, Westport, CT, 1982.
2. S. Daniele, I. Lavagnini, M.A. Baldo and F. Magno, *J. Electroanal. Chem.*, **404**, 105, 1996.
3. S. Daniele, I. Lavagnini, M.A. Baldo and F. Magno, *Anal. Chem.*, **70**, 285, 1998.

THE DEVELOPMENT OF A ONE-STEP DIAGNOSTIC SYSTEM FOR CYSTIC FIBROSIS (CF) USING A POTENTIOMETRIC MICRO-ELECTRODE SENSOR ARRAY

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Sweat analysis is attractive as a non-invasive diagnostic procedure, particularly in the diagnosis of Cystic Fibrosis [1]. Current methods of sweat collection and analysis are laborious and expensive however. In this study we employ a multi-sensor array in the analysis of both CF positive and negative sweat samples with a view to developing a simple, one-step screening process, incorporating sampling, analysis and diagnosis. The array is incorporated into a small and portable analysis system, it is compatible with existing products, and exhibits a rapid, stable and reproducible response. This diagnostic system has been employed in a series of clinical trials and clear differentiation between CF positive and normal sweat samples is exhibited.

In conjunction with the National Micro-electronics Research Centre (NMRC) work is underway to re-design and re-engineer the array to further miniaturise the system and reduce the required sample volumes to facilitate replicate analyses on raw sweat samples without the need for sample pre-treatment or dilution.

Reference

1. R. Darling, P. Di Sant'Agnese, G. Perera, et al.; Am. J. Med. Sci., 225 (1953) 6

DETERMINATION OF ADDITIVES AND MONOMERS IN STYRENE AND STYRENE-BASED POLYMERS USING CYLINDRICAL MICROELECTRODES

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Cylindrical microelectrodes various milimeters in length are useful for electrochemical measurements in resistive media. The micrometric radius of such electrodes allows the maintenance of low ohmic drop and diffusional characteristics of microelectrodes. Moreover, the relatively high currents measured increases sensitivity and permits the use of conventional instrumentation. These properties make possible that these microelectrodes are used for the direct analysis of organic analytes extracted in organic solvents of low permittivity.

A method has been developed for the determination of p-tertbutylcatechol (pTBP), an antioxidant added to styrene, using cylindrical carbon fibre microelectrodes (CFMEs) (8 μ m 4, 8 mm length). Furthermore, under similar experimental conditions, a method for the determination of styrene was also developed. Analytical solutions were prepared in acetone-0.01 mol l⁻¹ NaClO₄ due to the high solubility and good electrochemical behaviour of both compounds in this solvent. Scarce electroanalytical work have been made in acetone, in spite of its permittivity value (γ = 21.5) and moderate conductivity. All experiments were carried out in a two-electrode cell.

Cyclic voltammograms from 2.0 x 10⁻⁵ mol l⁻¹ pTBP solutions showed a sigmoidal response typical of microelectrodes. Moreover, at low potential scan rates (5 mV s⁻¹), the direct and reverse sweeps are coincident, which characterize reversible systems. SWV was used for the determination of the antioxidant using $f=25\text{Hz}$, $E_{sw}=25\text{mV}$ and $\phi E_s=2\text{mV}$. The net current voltammogram showed a well defined oxidation peak at 1.3 V. A linear calibration graph was obtained in the 1.0x10⁻⁶-1.0x10⁻⁴mol l⁻¹. The RSD was of 2.4 % and the detection limit was 4.3x10⁻⁷mol l⁻¹ antioxidant. Commercial styrene samples containing a 0.005% antioxidant were analyzed with good results, the mean value being 0.0047 $\pm$ 0.0003 % (n=10). Net current SW voltammograms from styrene solutions showed an oxidation peak at $E_p=1.8$ V. A linear calibration graph in the 1.0x10⁻⁶-1.0x10⁻⁴mol l⁻¹ concentration range was obtained, with a slope of 2.4 x 10⁴ μ A mol⁻¹ l. A much better sensitivity than that obtained from other methods for styrene was achieved. Simultaneous determination of both analytes, and the analysis of styrene-based polymers have also been carried out.

**ELECTROCHEMICAL BEHAVIOUR OF POTASSIUM FERROCYANIDE
AT SINGLE MICROMETRIC PARTICLES OF PLATINUM.
COMPARISON WITH AN ULTRAMICROELECTRODE**

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During previous studies on the electrochemical behaviour of conducting minerals as silver chalcogenides or pyrite, we have shown that it was possible to get similar results to these obtained with carbon paste electrodes by considering voltammograms at a single micrometric particle of the mineral [1][2]. The developed technique, by adaptation of the Bursell method [3], consists of using as working electrode a conducting particle placed on a glass frit soaked by the solution by capillarity. The electric contact with the particle is made with a carbon fibre.

During cyclic potential sweepings, with scan rates (v) of some mV/s, soluble species generated at the mineral particle showed peaks during reversal scans, despite the small particle size (some tens of μm). However, peakshape voltammograms are not observable with such a small v at a classic ultramicroelectrodes (UME) of similar size and used under conventional conditions. To understand the phenomena, we have considered the electrochemical behaviour of a model soluble electroactive species - potassium ferrocyanide - at non electroactive particles of platinum or gold.

A systematic study of the voltammograms characteristics (peak current, separation of potentials between anodic and cathodic peaks and charge exchanged) as a function of v and of the porosity of the glass frit has been undertaken. The analysis of results shows that the experimental curves do not correspond to any known voltammetric technique i.e. at the steady state, cyclic or in thin-layer voltammetry but to the combination of the three. Indeed, the effect of the platinum particle wetting is the formation of a meniscus of solution that behaves as a thin-layer. The system can be modelled as the sum of two components: an UME and a thin-layer. This remains true as long as the diffusion layer thickness remains wider than the thin-layer. When v becomes high enough for the diffusion layer thickness to become smaller than that of the thin layer, the system varies with v according to the cyclic voltammetry theory.

Another advantage of this device is that it allows to have particular UME made of any conducting material which can operate *in situ* without external disruption, even in the absence of a supporting electrolyte.

References

- [1] M. Perdicakis, N. Grosselin and J. Bessière *Electrochimica Acta*, 42 (1997) 3351
- [2] M. Perdicakis, N. Grosselin and J. Bessière *Anal. Chim. Acta* 305 (1999) 467
- [3] M. Bursell and P. Björnbom, *J. Electrochem. Soc.*, 137 (1990) 363

**ANALYTICAL PROCEDURES FOR THE ELECTROCHEMICAL
DETERMINATION OF HEAVY METALS AND HYDRONIUM IONS IN
MICROVOLUMES OF NATURAL WATER**

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For the further understanding of wet deposition from the atmosphere detailed investigations about the pollutant burden of rain water in dependence on location, time, and meteorological conditions are necessary. Especially, efficiency and mechanisms of wash-out effects are of interest. This problem represents a challenge for the design of microanalytical procedures. Because of their power of detection, sensitivity, and miniaturization potential electroanalytical methods should be well suited for the measurement of heavy metals and other rain water constituents in small droplets.

Therefore, voltammetric procedures were developed by using gold, platinum, and glassy carbon microelectrodes including appropriate measuring cells for the determination of Pb, Cd, Zn, and Cu in microvolumes of water and even in single raindrops. The analytical procedures were validated by the application of a completely different analytical approach, namely electrothermal vaporization-inductively coupled plasma-mass spectrometry. Moreover, pH measurements were performed in very small volumes of rain water by using appropriately designed pH sensors with ion-selective field effect transistors. Corresponding experimental results will be presented and discussed with respect to their environmental significance.

ELECTROANALYSIS WITH NANO-ELECTRODES ENSEMBLES

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A new type of electrode of nanoscopic dimensions, called nanoelectrodes ensembles, (NEEs), has been introduced recently[1]. These electrodes are prepared by using nanoporous ultrafiltration membranes as templates for the electroless deposition of gold nanowires with exposed nanodisc surfaces of approx. 30 nm diameter. Voltammograms obtained at such NEEs are peak-shaped with faradaic peak currents proportional to the overall geometric area of the ensemble while the capacitive current (which in this case is the main component of the noise) depends only on the active nanodisc area. This gives very favourable signal to noise ratios and allows one to obtain well resolved cyclic voltammetric responses even at low solution concentrations, with detection limits about two orders of magnitude lower than those obtained at conventionally sized electrodes. The analytical performance can be further improved by using polymer coated NEEs [2].

In this communication the analytical performance of NEEs, in terms of background noise and detection limits, are compared with those of conventionally sized electrodes. The examined analytes are some redox mediators, such as phenothiazines, viologens, ruthenium complexes and ferrocene derivatives. Finally, the possibility to use NEEs in combination with a new sensitive electroanalytical technique, namely multiple square wave voltammetry [3], will be presented.

References

1. Menon, V. P., Martin, C. R., Anal. Chem. **67** (1995) 1920.
2. Ugo P., Moretto, L.M., Bellomi S., Menon, V.P., Martin, C.R., Anal. Chem. **68** (1996) 4160.
3. Moretto, L.M., Ugo, P., Lacasse, R., Champagne, G.Y., Chevalet, J., J. Electroanal. Chem., **467** (1999) 184.

EFFECT OF SUPPORTING ELECTROLYTE DEFICIENCY IN VOLTAMMETRIC DETERMINATION OF EQUILIBRIUM CONSTANTS

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Application of microelectrodes allows the use of voltammetric methods in the environments traditionally considered to be unsuitable for electrochemistry. A well-known example are the media with deficiency of supporting electrolyte. Such situation is often met in environmental analysis (pore water, rainwater, snow melt) and in supramolecular chemistry. The addition of a large amount of supporting electrolyte may change the chemical equilibrium to such an extent, that the obtained experimental results cannot be used to draw conclusions about the original samples.

The extensive literature on the voltammetric determination of homogeneous equilibrium constants is almost exclusively devoted to situations when supporting electrolyte is present in significant excess. Under such conditions the transport of all species is controlled by diffusion and the migrational phenomena are negligible. The voltammetric theory for excess supporting electrolyte cannot be applied to our purposes. In fact, only contemporary digital simulation strategies are able to cope with migrational systems. They are effective and therefore the level of supporting electrolyte is not a limiting factor any more. The studies of homogeneous equilibria at low supporting electrolyte / analyte concentration ratios become feasible.

In our contribution we focus on the determination of complex formation constants. Theoretical simulations for various types of complexes consisting of a cation and a macrocyclic ligand are presented, compared and discussed.

EXPLOITATION OF CYCLIC VOLTAMMETRY AND STRIPPING VOLTAMMETRY FOR TRACE ANALYSIS

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The determination of traces and ultratraces of dissolved heavy metals and other inorganic ions in solution is a major field of application for various electroanalytical methods. In the past techniques based on the measurement of Galvani potential differences, faradaic currents or charges and conductivity of solutions have been developed and optimized. For the purpose of modern approaches in analytical chemistry such as speciation and the increasing demands of quality assurance one has to develop alternative detection modes also in this classic field of electroanalysis.

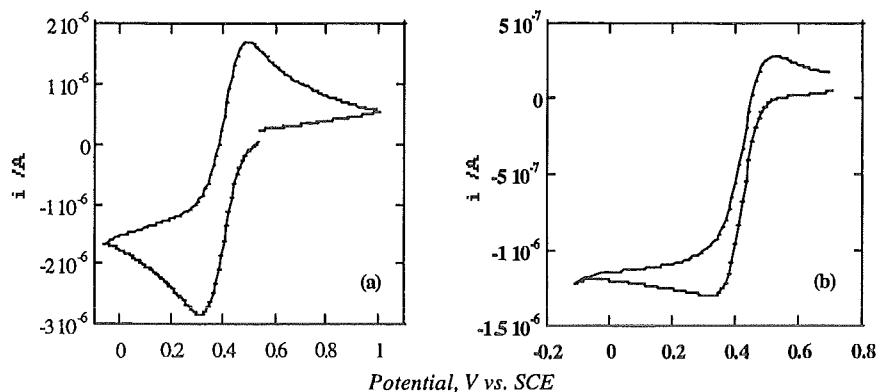
The phenomenon of changing surface resistivity due to adlayer formation at the metal/solution interface is known from surface physics at silver single crystal surfaces. We are exploiting this effect for the purpose of an alternative quantification principle at nanometer thin polycrystalline electrodes. Fundamental investigations about the potential dependence of metal deposition and dissolution can be performed by cyclic voltammetry, that means the measurement of surface resistance-potential curves. The trace analysis of environmentally relevant heavy metal ions in aqueous solution was achieved by stripping voltammetry. The investigation of various excitation techniques and evaluation modes will also be discussed in this contribution.

ELECTROCHEMICAL BEHAVIOUR OF A NAFION®-COATED DOUBLE BAND MICROELECTRODE LOADED WITH FERRIC CATIONS

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The electrochemical responses of Pt-bands and double-band ultramicroelectrodes were performed with electrodes previously coated by a Nafion® membrane containing ferric ion species. Nafion® is an excellent cation exchange material leading to electrostatic binding between sulfonate groups and Fe(III)/Fe(II) species. As a consequence diffusion transport in this polymer is controlled mainly by combination of the physical displacement of the redox species and charge hopping. The cyclic voltammograms at coated microbands and their associated chronoamperograms were carried out for different thickness of the loaded film. The diffusion process in the film (Fig a) was evidenced by comparison to the measurements obtained at an uncoated microband electrodes in a ferric ion solution (Fig b).



Figures: (a) Cyclic voltammogram of the Nafion®-coated microband loaded with ferric ion in solution containing only H_2SO_4 0.1M. Scan rate $5mV s^{-1}$. (b) Cyclic voltammogram of a Pt-microband without polymer in a 10mM Fe(III), H_2SO_4 0.1M solution. Scan rate $5mV s^{-1}$.

The band alone as well as the generator-collector responses depended on the presence of alcohols in the cell. This constitutes an interesting result in view of the conception of new kind of artificial-nose devices.

Simulations were performed to account for the diffusional properties observed at single-bands as well as for double-band coated-electrodes operated in collector-generator mode. A good agreement was found between theoretical and experimental results according to the film thickness.

ELECTROCHEMISTRY OF MICROPARTICLES OF TRIS(2,2'-BIPYRIDINE)RUTHENIUM(II) HEXAFLUOROPHOSPHATERamasamy Ramaraj¹, Christian Kabbe and Fritz Scholz²¹From School of Chemistry, Madurai Kamaraj University, Madurai-625 021, India.²Ernst-Moritz-Arndt-Universität Greifswald, Institut für Chemie und Biochemie
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The electrochemical behaviour of tris(2,2'-bipyridine)ruthenium(II) hexafluorophosphate (Ru(II)) microparticles immobilised on a graphite electrode and adjacent to an aqueous electrolyte solution, has been studied by cyclic voltammetry and an in situ spectroelectrochemical technique. The solid Ru(II) complex exhibits one reversible redox couple with a formal potential (E_f) of 1.1 V vs. Ag/AgCl. The continuous cyclic voltammetric experiments showed that the Ru(II) microparticles are stable during the electrochemical conversions. The in situ spectroelectrochemical study showed that the absorbance at 463 nm decreased due to the oxidation of Ru(II) to Ru(III). Upon reduction, the growth of absorbance at 463 nm was observed due to the formation of Ru(II) complex and this process was reversible.

MAPPING CONCENTRATION PROFILES WITHIN A STEADY STATE DIFFUSION LAYER USING AN ULTRAMICROELECTRODE

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Application of an electrochemical perturbation at an electrode results in the spatial structuring of the substrate and products concentration profiles near the electrode surface. Some groups [1-3] have already attempted to monitor experimentally such concentration profiles. We wish to demonstrate that a suitable alternative consists in performing a series of potentiometric [4] and chronoamperometric measurements with an ultramicroelectrode probe within the steady-state diffusion layer of another electrode operated potentiostatically. From the experimental potential variations, which result from a combination of a pure electrochemical component and ohmic drop, concentration profiles of the electroactive species present within the diffusion layer can be reconstructed by application of the Nernst law.

On the other hand, the determination of current variations inside the steady-state diffusion layer created by a larger electrode correlates directly to the concentration profiles of the electrochemical species under investigation.

The validity of both methods is demonstrated experimentally by the study of the one-electron reversible oxidation of the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ couple in aqueous KCl solutions. These methods are then applied to examine the specific structuration of diffusion layers, which result from the involvement of a comproportionation reaction during the second reduction of tetracyanoquinodimethane (TCNQ) in DMF.

References

- [1] R.C. Engstrom, T. Meaney, R. Tople, R.M. Wightman, *Anal. Chem.* 59 (1987) 2005.
- [2] I. Frateur, E. Bayet, M. Keddad, B. Tribollet, *Electrochem. Commun.* 1 (1999) 336.
- [3] C. Amatore, F. Bonhomme, J-L. Bruneel, L. Servant, L. Thouin submitted to *Electrochem. Commun.*
- [4] C. Amatore, S.Szunerits, L. Thouin, submitted to *Electrochem. Commun.*

Poster Contributions

Session C

STUDIES OF ORGANOSULFUR FILMS ON GOLD ELECTRODES FOR METAL ION DETECTION

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We are interested in the development of thin organo-film electrodes for applications in metal ion detection. Here we will present our results on the preparation and behaviour of films of amino acids and short chain mercaptoalkane sulfonates.

The adsorption of L-cysteine on gold electrodes was studied by the methods of electrochemical oxidative desorption and Cu^{2+} complexation.¹ Films prepared from L-cysteine had a lower surface coverage than those from L-cysteine. However, both the L-cysteine- and the L-cysteine-derived electrodes were capable of complexation of Cu^{2+} ions from solution, which were then detectable by cyclic voltammetry: detection of Cu^{2+} down to 10^{-7} M was possible.

The ability of spontaneously adsorbed monolayers possessing terminal sulfonate groups to prevent electrode surface fouling by surfactant-containing solutions was examined.² Films of 3-mercaptopropane sulfonate (MPS) on polycrystalline gold electrodes were prepared from acidic solution and characterised by reductive desorption. The voltammetric reduction of lead(II) ions at such electrodes revealed an enhanced current for the apparent underpotential deposition (upd) compared to the current observed at a clean polycrystalline gold electrode. The enhanced upd current was maintained in the presence of bovine serum albumin (BSA), indicating the ability of the MPS film to prevent adsorption of BSA on the gold electrode and using the enhanced upd current, 1 μM Pb^{2+} could be detected in solution using square wave voltammetry.

Finally, we have commenced study of the upd of other metals on gold electrodes (e.g. copper on gold is a classical example) coated with MPS. We will present our latest results and illustrate the possible analytical utility of such behaviour.

References

1. D.W.M. Arrigan & L. Le Bihan, A study of L-cysteine adsorption on gold via electrochemical desorption and copper(II) ion complexation, *The Analyst*, **124** (1999) 1645-1649.
2. D.W.M. Arrigan, L. Le Bihan & M.J. Pickup, Apparent enhanced underpotential voltammetry of lead(II) at a spontaneously adsorbed monolayer-coated gold electrode, *The Analyst*, **124** (1999) 1797-1802.

DETECTION OF HYDROCARBONS IN AIR BY ADSORPTION ON PT-ELECTRODES USING A MODIFIED ANODIC STRIPPING PROCEDURE

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Many organic compounds such as benzene, its derivatives and simple halogenated hydrocarbons cannot be detected by usual amperometric sensors. Their detection, however, is possible by means of their adsorption at a Pt-sensor electrode. The charge is automatically determined during a subsequent sweep to potentials above 1 V (RHE). It is corrected for oxygen adsorption and serves as a measure for the substance concentration. A special potential program serves to repeatedly strip the adsorbate from the surface, thus allowing the continuous detection of such compounds [1].

The linearity of the sensor signal with concentration depends on the time independent adsorption rate. This can be maintained only as long as the coverage of the electrode remains low. Therefore, the change of the electrode capacity due to adsorbate formation is continuously monitored by ac -measurements. This is possible despite of the high oxygen reduction currents at the adsorption potentials [2]. The adsorption is terminated and the oxidation is started when the electrode capacity has decreased below a chosen value. In this way, the endpoint of the adsorption can be controlled by a preset coverage rather than by a preset adsorption time. Thus, the linear response of the sensor can be extended to higher concentrations without sacrificing sensitivity in the lower concentration range. For toluene, a linear signal response was found between 5 and 100 ppm and higher, thus covering a wide range around the threshold limit value of 50 ppm. The potential program allows the discrimination against substances which are oxidized below 1 V (RHE) like CO, NO, and simple alcohols.

References

- [1] H. Baltruschat, I. Kamphausen, R. Oelgeklaus, J. Rose, M. Wahlkamp, *Anal. Chem.* 69 (1997) 743
- [2] R. Oelgeklaus, H. Baltruschat, *Sensors and Actuators B* 42 (1997) 31.

MERCURY ELECTRODES MODIFIED WITH SUPERCOILED DNA: ELECTROCHEMICAL PROBES OF DNA INTERACTIONS AND DAMAGE

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Damage to DNA may result in serious disturbances of the cell functions, including mutations or malignant transformation. Because of close relation of DNA damage to human health, development of rapid and sensitive analytical methods capable of detection of DNA damage (or DNA damaging agents) is important.

DNA damage by chemical or physical agents frequently involves interruptions of DNA sugar-phosphate backbone (strand breaks, sb). Adsorption/desorption behavior of supercoiled (sc) DNA (not containing sb) at mercury electrodes strongly differs from that of DNA molecules containing free ends (open circular, oc, or linear DNAs) [1]. In addition, a restricted reducibility of bases in scDNA (as compared to those in DNA containing sb) at the mercury electrode was observed [2]. It has been shown that surface-confined scDNA can be nicked by chemical nucleases, e.g. hydroxyl radicals generated in Fenton reactions mediated by transition metal ions in the presence of hydrogen peroxide and a reducing agent. Cleavage of immobilized scDNA at the mercury electrode mediated by transition metals can be facilitated by sufficiently negative electrode potential in absence of reducing agents. Besides low molecular mass DNA damaging agents, scDNA adsorbed at electrically charged mercury surface can be attacked by deoxyribonuclease I [3]. Kinetics of this reaction is strongly potential-dependent, suggesting an influence of the electrical field close to the electrode surface on the DNase I-DNA interaction.

We used mercury film plated on a glassy carbon electrode for the measurements of redox as well as tensammetric signals of DNA, RNA and synthetic nucleic acid analogues. Behavior of nucleic acids at the mercury film electrode (MFE) was similar to that observed previously at HMDE. Formation of single- or double- strand breaks in DNA was detected by means of AC voltammetry at the MFE. MFE modified with scDNA was used as a biosensor for the detection of DNA-cleaving species.

References

1. M. Fojta and E. Palecek, *Anal. Chim. Acta* (1997) 342, 1.
2. M. Fojta, L. Havran and E. Palecek, *Electroanal.* (1997) 9, 1003.
3. M. Fojta, T. Kubicarova and E. Palecek, *Electroanal.* (1999) 11, 1005.

VOLTAMMETRIC DETECTION OF HEAVY METALS AFTER ACCUMULATION ON POLYSILOXANE-IMMOBILIZED AMINE LIGANDS

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The chemical modification of conventional electrodes allows to bring additional reactivity and properties which can be exploited, for example, to accumulate analyte species or to impart catalytic activity. In particular, carbon paste is a versatile electrode material which can be modified by direct mixing to an appropriate component [1]. This approach is well suited to non conductive modifier as silica or zeolites [2, 3]. After having exploited the accumulation of Cu^{II} and Hg^{II} , from an ammoniacal medium, on various silica surfaces for the voltammetric detection of these analytes using silica-modified carbon paste electrodes [4, 5], we provide here an evaluation of a new electrode modifier made of amine ligands covalently immobilized on silica gel. In this case, the accumulation of the metal analytes would not require the addition into the solution of a reactant enabling their fixation on the silica surface.

The accumulation of Cu^{II} and Hg^{II} on silica gel grafted with aminopropyle groups (ORMOSIL: organically modified silicate) was found to depend strongly on pH and chloride concentration (especially for Hg^{II}). Two mechanisms were observed. In the absence of chloride, both Cu^{II} and Hg^{II} species can be adsorbed on the ORMOSIL by complexation with amine ligands, this bonding being however prevented at high pH because of the formation of hydrolysis products of the analytes. In the presence of chloride ($> 0.5 \text{ M}$), we have observed the accumulation of HgCl_4^{2-} on the ORMOSIL in acid medium, i.e. where the surface amine groups are protonated (R-NH_3^+), according to an ion exchange process. The preconcentration effects were then exploited for the voltammetric determination of Cu^{II} and Hg^{II} . The influence of several experimental parameters was studied to optimize the electrode response.

References

- [1] A. Walcarius, *Electroanalysis*, **10** (1998), 1217.
- [2] A. Walcarius, *Electroanalysis*, **10** (1998), 1217.
- [3] A. Walcarius, *Anal. Chim. Acta*, **384** (1999), 1
- [4] A. Walcarius, C. Despas, P. Trens, M.J. Hudson, J. Bessière, *J. Electroanal. Chem.*, **453** (1998), 249.
- [5] A. Walcarius, C. Despas, J. Bessière, *Anal. Chim. Acta*, **385** (1999), 79

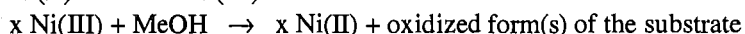
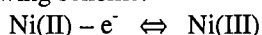
OXIDATIVE ELECTROCATALYTIC DETERMINATION OF ORGANIC AND INORGANIC SUBSTRATES AT ELECTRODES MODIFIED WITH NICKEL-BASED HYDROTALCITES

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We have tested previously¹ the experimental conditions for utilising a glassy carbon (GC) electrode modified with a film of [Ni/Al-Cl] HT, obtained by droplet evaporation of 20 µl of a colloidal solution. The possibility of using similar modified electrodes to detect alcohols, through an electrocatalytic oxidation, has also been demonstrated.² The electrocatalytic mechanism involves the Ni(II) centres as redox mediators, according to the following scheme:



The coatings obtained by the simple procedure described were however poorly reproducible and scarcely stable from a mechanical point of view, so that the electrodes could not be proposed as practical devices. It is evident that an amperometric sensor based on a modified electrode, to be used for analytical applications in real systems, should possess chemical and mechanical stability, long lifetime, simple regenerability of the coating, and should give stable and repeatable responses. Electrodes with best performances with this respect have been constructed by inserting a metal wire (Pt, Cu or GC) into a glass tube whose end tip was filled with a HT/epoxy resin paste. This was then ground on silicon carbide papers until appearing as a section of the metal (or GC) wire, surrounded by the HT/epoxy solid mixture; this configuration constituted the actual electrode surface, which was finally polished to a mirror-like surface. Cyclic voltammograms were recorded in NaOH 0,1 M: the anodic-cathodic signal, ascribed to oxidation and subsequent reduction of nickel centres in the brucite layers, appeared very stable for many days. Organic and inorganic substrates such as alcohols, alditols, sugars, thiosulphates, sulphites have been added to the alkaline solution in order to test the electrocatalytic response in the presence of different amounts of substrates. The 'best' signals were obtained when the inner wire was made of Pt or of GC, since these materials do not interfere with the oxidation of the substrates catalysed by the nickel centres. The height of the anodic peak increases at increasing the substrate concentration and wide ranges of linearity and high reproducibility of the responses are obtained for a wide series of substrates. For the most part of these the linearity range was 5×10^{-5} – 10^{-2} M and the detection limit was about 10 µM.

References

1. B.Ballarin, R.Seeber, D.Tonelli, A.Vaccari, J.Electroanal.Chem. 1999, 463, 123
2. B.Ballarin, R.Seeber, D.Tonelli, C.Zanardi, Electroanalysis, in press.

**CHARACTERIZATION OF THE CAPACITANCE AND QUALITY OF THIOL
BASED SELF ASSEMBLED MONOLAYERS BY IMPEDANCE SPECTROSCOPY
AND CYCLIC VOLTAMMETRY**

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Capacitive electrochemical sensors having the recognition layer immobilized via a self assembled monolayer have recently been shown to reach detection limits in the fM range for antigens and heavy metals. The performance of these sensors is, however, critically dependent on the quality of the electrode surface and the insulating properties of the self assembled monolayer.

In this contribution, the capacitance and insulating properties of self assembled monolayers of thiols on gold electrodes is discussed. Very flat vapor deposited gold surfaces were used to obtain high quality monolayers intended to serve as a base for a oligonucleotide sensor based on capacitance measurements. The influence of the length of the thiols and presence of functional groups on the terminal end on the monolayer thickness and capacitance was studied by ellipsometry and impedance spectroscopy. The quality of the monolayers, i.e. the presence of defects, was investigated by cyclic voltammetry.

Monolayers with very good insulating properties were obtained when a mixture of two thiols in ethanol, for example HS-C₁₁H₂₂-OH and HS-C₁₅H₃₀-COOH, was used during the self assembly. The number of defects were in this case less compared to if the monolayer consisted of only one of the thiols. The capacitance and average thickness of these mixed monolayers were found to be dependent on the mix ratio of the thiols in the ethanol solution. These results and the distribution of the mixed thiols on the electrode surface together with the coupling of a single stranded oligonucleotide to a -COOH terminated thiol will be further discussed in the poster.

SOME NITRIDES OF TRANSITIONAL METALS AS NEW MATERIAL FOR CHEMICAL SENSORS

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Compounds of transitional metals as nitrides, sulfides, carbides and so on are of potential interest in electroanalytical methods because of their high electrical conductivity, chemical and electrochemical stability. Many of these materials are produced as powders with a specific electrical resistance (ρ) too high for practical usage ($\rho \sim 10^6 \Omega \text{ cm}$). We proposed and studied a new method of electrode preparation by pressing at room temperature the mixture of nitride and a solution of a polymer in the frame from the same polymer in the laboratory hand device at a relatively small pressure[1-3]. We studied TiN, TaN, NbN composite electrodes in the pH range of 1 to 9. In this pH range the windows are in 0.1 M HNO_3 for TiN from -0.6 to 1.6 V, for TaN from -0.7 to 1.7 V, for NbN from -0.6 to 1.8 V. In 0.1 M KNO_3 for TiN from -0.8 to 1.2 V, for TaN from -1.15 to 1.4 V, for NbN from -1.0 to 1.6 V. In 0.05 M $\text{Na}_2\text{B}_2\text{O}_7$ for TiN from -1.0 to 1.3 V, for TaN from -1.3 to 1.4 V, for NbN from -1.2 to 1.4 V (Ag/AgCl sat. reference electrode). These experiments show that the windows of the MeN electrodes in the anodic region are approximately 0.2 -0.3 V wider than classical glassy carbon (GC). This allows to determine some compounds with high overvoltages. For example we use a TiN electrode for the determination of thiols as monothioglycerol (MTG) and thioacetic acid (TAA). There are peaks of MTG at 0.97 V and of TAA at 1.01 V in acetic buffer with pH-5; in the same conditions there are no peaks for MTG and TAA with the use of GC electrode. The calibration curves for MTG in the range of 10-100 μM and for TAA in the range 7 - 100 μM are linear.

References

1. B. Filanovsky, Y. Tur'an, I. Kuselman, T. Bourenko, A. Shenhar, Anal. Chim. Acta. 364 (1998) 181
2. B. Filanovsky, Anal. Chim. Acta 394 (1999) 91. 3. T. Bourenko, B. Filanovsky, A. Levitsky, Anal. Chim. Acta (in press).

EQCM AS A TOOL TO CHARACTERIZE SELF-ASSEMBLED MONOLAYERS OF THIOCTIC ACID ON GOLD

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Self-assembled monolayers (SAMs) of thiols, sulfides, and disulfides with a suitable functional group can be used as intermediate layers for the attachment of a wide range of molecules, including enzymes and antibodies, to a gold substrate, resulting in a (bio)sensor. The electrochemical quartz crystal microbalance (EQCM) usually consists of a quartz disk plated with gold electrodes, in which the gold film in contact with a solution is used as the working electrode in an electrochemical cell.

We used a 10 MHz EQCM to monitor the formation of a SAM of thioctic acid, and the derivatization of its carboxylic acid group with antibodies. Experiments have been done both in batch, and in a home-made flow-through cell of the free wall-jet type. A combination of amperometry and measurement of the resonance frequency of the quartz crystal has been used to characterize the performance of the flow cell. Cyclic voltammetry, combined with resonance frequency measurements were used to characterize the state of the gold surface. AC-impedance techniques were used with a concomitant measurement of the resonance frequency of the crystal to monitor the formation of the SAM from aqueous solution (phosphate buffer pH 7.4), and its derivatization in a flow system.

Quartz crystals with a chromium and a titanium adhesion layer have been investigated.

It was found that the adhesion layer between quartz and gold plays an important role, both in the electrochemical, and in the QCM-characteristics of the gold thin-film electrode. Measurements in hexacyanoferrate solutions revealed a photochemically induced etching of gold, probably through release of cyanide. It has been observed that also the chloride anion in PBS is able to induce relatively large frequency shifts.

ELECTRICALLY HEATED BIOSENSORS

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In nucleic acid analysis and related techniques, temperature changes play an important role. In hybridisation experiments, e.g., double strings of probe molecules have to be "molten" (transformed to single strings) by mild heating as a premise for the formation of complexes with the target molecules. Other examples of heat application are the controlled release of DNA or RNA from natural cells, or further the release of trapped target molecules from the double or triple string formed in hybridisation process.

Directly heated microelectrodes (Hot-Wire or Hot-Layer electrodes) can be used as electrochemical sensors, with nucleic acids or for nucleic acids, including hybridisation sensors. Their surface temperature can be controlled precisely by application of an electric current, rather than thermostating a solution volume [1]. Consequently, the whole process can be automated very easily.

The bulk solution is not heated in the technique described here, thus delicate substances are left unaffected by increased temperature. The temperature range necessary for biologically active substances is well suited for a highly efficient control at electrically heated electrodes. Stability and precision is comparable, in this range, with thermostating, but changes can be applied much faster.

These new electrodes are useful for hybridisation analysis [2]. In this case, fragments of natural or artificial DNA are immobilised at the electrode surface or incorporated in the electrode. Electrochemical processes are similar to that with common electrochemical probes, but temperature can be varied or even switched faster and more easily.

A different application of our new electrodes was trace determination of nucleic acids by adsorptive stripping. Increased temperature at the electrode surface resulted in a much higher analytical signal, obviously caused by a drastic increase of adsorption rate. The method proved useful to investigate adsorption kinetics of large and complex molecules.

The preferred material for all electrodes was carbon, either in the form of thin layers made by the pyrolysis, of screen printed structures, or of heated carbon paste electrodes.

References

1. P. Gründler, A. Kirbs, *Electroanalysis* 11(1999)223
2. P. Gründler, G.-U. Flechsig, M. Jasinski, O. Korbut, J. Wang, DE Patent, reg. Dec. 15, 1999

ONE-STEP ELECTROPOLYMERIC COIMMOBILIZATION OF GLUCOSE OXIDASE AND HEPARIN FOR AMPEROMETRIC BIOSENSING OF GLUCOSE

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Sensing of glucose in biological fluids is extremely important for providing a tight diabetes control. Amperometric biosensors based on glucose oxidase have therefore attracted a major attention, recently also through the introduction of ultramicroelectrode transducers [1,2]. However, with implantable glucose biosensors designed for in-vivo monitoring in whole blood or in the interstitial fluid, fibrin formation and clotting upon exposure to blood represent one of the major problems.

In this work, electropolymerization has been used for the codeposition of glucose oxidase and heparin onto metal electrode transducers. Such electropolymeric co-entrapment within the nonconducting poly(1,2-phenylenediamine) (PPD) film imparts both biocatalytic and anticoagulation activities onto the transducer, and greatly improves the performance of the sensor after exposure to whole blood. Essentially identical glucose signals are observed before and after exposure to blood samples. Scanning electron micrographs after such exposure reveal no platelet deposition or formation of fibrin 'clot'. The effect of the heparin co-immobilization upon the glucose response is examined. Improved biocompatibility is reported also in connection to a needle-type carbon paste biosensor configuration. The simultaneous localization of the enzyme and heparin offers great promise for simplifying the preparation of enzyme electrodes and designing biocompatible implantable glucose biosensors.

References

- [1] J. Wang, Anal. Chem. 1998, 71, 328R.
- [2] X. Zhang, J. Wang, B. Ogorevc, U. E. Spichiger, Electroanalysis 11 (1999) 945.

POROUS SILICON AS BASE MATERIAL FOR SENSOR APPLICATIONS

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Due to the interesting luminescent properties, the formation of porous silicon has extensively been studied during the past years [1]. Moreover microstructuring of porous silicon is of great interest for sensor fabrication [2]. In this contribution the fabrication of a microreference electrode on the basis of a porous silicon substrate is described. N-type (100) silicon wafers were used to form a porous silicon layer. A silver/silverchloride reference electrode system was chosen as a first example and according to that silver/silverchloride layers were coated onto the porous substrate. A Nafion membrane was used as a finishing layer to diminish the washout of the electrolyte reservoirs.

Furthermore a throuetching process is described. The result of this process is a porous silicon substrate with a very large surface and crater-like structures. These structures can be useful as a base material for polymer or bioenzyme based sensors. The crater-like structures can be used as a reservoir for the sensor component and as a grip-improvement for the sensor material.

References

- [1] L. T. Canham, Appl. Phys. Lett., 57 (1990), 1046
- [2] M. J. Schöning, F. Ronkel, M. Crott, M. Thust, J. W. Schultze, P. Kordos, H. Lütth, Electrochimica Acta 42 (1997), 3185

ELECTROCATALYTIC REDUCTION OF HEMOGLOBIN AT TOLUIDINE BLUE/POLYPYRROLE FILM MODIFIED GOLD ELECTRODES

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Hemoglobin (Hb) is a tetramer heme protein composed of two β subunits and a carrier to store and transport oxygen in blood of vertebrate animals. It's content is related to many clinical diseases such as anemia, leukemia, heart disease, etc, thus, the determination of Hb concentration is very important in clinical medicine. In General, Hb has insufficient electrochemical response at a bare electrode due to the passivated adsorption of its insulated protein shells. Many chemically modified electrodes have been used to determine Hb an electrochemical method. Although the direct electrochemical determinations of some redox protein and small biomolecules can be achieved at the polypyrrole film modified electrode, the catalytic ability is weak due to the poor electroactive polypyrrole film.

This work obtains a toluidine blue (TBO) monomers mingled polypyrrole film which is formed at a gold electrode surface by using cyclic sweep between -600 and +600 mV for 40 min in pH 7.0 phosphate buffer containing 6 mM toluidine blue + 0.03 M KCl + 0.3 M pyrrole. The film possesses good conductivity, and shows a pair of well-defined peaks with a formal potential of about -250 mV versus SCE at pH 7.0. With increasing scan rate the peak currents increase linearly and the cathodic and anodic peak potentials shift in the opposite directions. The peak-to-peak separation (ΔE_p) of 150 mV at 30 mV/s is probably ascribable to the immobilized TBO monomers in various orientations. The excellent electrocatalytic behavior of Hb is observed in pH 7.0 PB at the TBO/polypyrrole modified electrode. A considerably fast catalytic response of Hb is obtained, with a 95 % of steady-state current being achieved in less than 15 s at the applied voltage of -300 mV. The calibration range is from 0.6 μ M to 0.1 mM with a linear relationship between 0.6 μ M and 30 μ M mM ($R = 0.997$). The detection limit was estimated to be 0.25 μ M at a signal-to-noise ratio of 3. The sensor showed good reproducibility for the determination of Hb concentration in the linear range.

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ELECTROCHEMICALLY-INDUCED DEPOSITION OF ENZYME-CONTAINING FILMS AS A BASIS FOR THE REPRODUCIBLE PREPARATION OF AMPEROMETRIC BIOSENSORS

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A prerequisite for the construction of amperometric biosensors is the controlled and reproducible immobilisation of enzymes on an electrode surface preserving a maximum of the enzymatic activity. In addition, the fabrication of biosensors especially miniaturised biosensors requires non-manual deposition techniques which allow to predefine the immobilisation site. Previously, it has been demonstrated that the electrochemical induced formation of enzyme containing films on an electrode surface such as electrophoretic accumulation [1] or polymerisation [2] can be used as non-manual immobilisation procedure. However, most of these techniques described so far are complicated and time consuming due to necessary purification steps for the preparation of the monomer solutions, removal of oxygen etc.

In this communication, a new, simple and fast procedure to produce enzyme-containing polymer films will be presented which is based on the entrapment of the biological recognition element during an electrochemically-induced formation of a polymer hydrogel exclusively on the electrode surface. First results concerning the properties of the obtained biosensors using glucose oxidase as a model for biological recognition elements will be discussed mainly focusing at:

- the control of the immobilisation reaction and related sensor characteristics
- the construction of multi-parameter biosensor arrays
- the formation of anti-interference multilayers
- strategies for the formation of mediator-modified polymer films.

References

- [1] D. J. Strike, N.F. de Rooji, M. Koudelka-Hep, *Biosens. & Bioelectr.* **10** (1995) 61.
[2] W. Schuhmann, *Mikrochim. Acta* **121** (1995) 1.

VOLTAMMETRIC STUDIES OF TRANSPORT OF ANALYTES IN POLY(N-ISOPROPYLACRYLAMIDE-*co*-ACRYLIC ACID) GELS SWOLLEN BY METHANOL

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The electrooxidation of methanol at platinum microelectrodes in poly(N-isopropylacrylamide-*co*-acrylic acid) (NIPA-AA) gels was studied in a function of temperature. Diffusion coefficients of methanol in NIPA-AA gels of various copolymer concentrations were determined from the steady-state voltammetric currents over the temperature range 5 - 55 °C. The data were analyzed in terms of the Arrhenius-like equation. Transport parameters (diffusion coefficients and activation energies of diffusion) were compared to those for undiluted methanol, and related to the transport properties of uncharged probe molecules of 1, 1' - ferrocenedimethanol in both liquid and gel media. Diffusion of uncharged species, methanol and 1, 1' - ferrocenedimethanol, in the gels was as fast as in liquid media, with diffusion coefficients close to $1 \times 10^{-9} \text{ m}^2/\text{s}$ for both species at 25 °C.

The activation energy of diffusion for methanol and 1, 1' - ferrocenedimethanol determined in the gels was smaller than those observed in liquid medium. This is probably due to a decrease in local viscosity of the gels during the oxidation process caused by the condensation of ions on the charged fragments of the polymeric network (carboxylic groups of acrylic acid). The calculated activation energies do not depend on the copolymer concentration in the range 1.3 – 2.5. The obtained results reveal that enormous macroscopic viscosity of the gel has a very small effect on the transport parameters of the uncharged species studied in the non-aqueous solvent.

The phenomena observed indicate that there is a real possibility of using microelectrodes immersed into gels for analytical purposes.

SOLID CARBON PASTE ELECTRODE BASED ON PHENOTHIAZINE AND HORSE RADISH PEROXIDASE

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The solid paraffin/graphite matrix (SPG) has been shown to be attractive for enzyme and redox mediator immobilization. The mild temperature (50 °C) used for mixing the different components appears to have no detrimental effect on enzyme stability at least for the two enzymes investigated: tyrosinase and peroxidase.

Electrochemical biosensors based on SPG offer interesting analytical properties in terms of stability and reproducibility of the assays comparing to a classical carbon paste electrode based on liquid paraffin. The biosensor is readily prepared and renewed i.e. similarly to the carbon paste electrode. Highly water soluble enzymes such as horseradish peroxidase (HRP) must be insolubilized by crosslinking with other proteins (e.g. Bovine Serum Albumin, or an other enzyme) for minimizing any leaking out of the electrode. Phenazine methosulfate and phenothiazine derivatives, such as methylene blue, are well-known as redox mediator for HRP, but they readily leak out into the aqueous buffer solution. The molecule phenothiazine is poorly water soluble, entrapped in the hydrophobic environment of the paste, it shows a reversible one-electron transfer and is readily oxidized by HRP. The resulting enzyme electrode has been shown to be very sensitive to hydrogen peroxide, allowing nanomolar concentrations to be readily determined. The performance of this biosensor towards hydrogen peroxide has been thoroughly investigated [1]. Dual enzyme configurations have been studied as well and applied to real samples of pharmacological interest.

Reference

1. S.Serradilla Razola, E.Aktas, J-C Viré, J-M Kauffmann, *Analyst*, 125 (2000) 79.

SORPTION OF MERCURY AND GOLD ON THE MONTMORILLONITE MODIFIED ELECTRODE

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Contribution discusses the possibilities of clay modified carbon paste electrodes (CPEs) in the investigation of ion exchange of various metals species, an attention is given to mercury and gold. The former studies performed by means of the clay CPEs [1,2] are extended.

Montmorillonite modified CPE was used for study of sorption of various Hg species in the dependence on pH. No sorption was supposed at low pH due to competition of H^+ ions for adsorption sites and due to releasing of Al ions from the clay structure. The sorption of Hg(II) in the form of its chlorocomplexes and acetate complexes on the montmorillonite showed to be strongly influenced by formation of hydroxocomplexes with increasing pH. Similar effects of formed hydroxocomplexes was also found in the case of the anionic exchange of $[AuCl_4]^-$ complexes. Open circuit sorption on the montmorillonite modified CPE in the medium of $NaClO_4$ showed increased sorption of Hg(II) with increasing pH. This pH dependence is quite different from the pH dependence in the acetate and chloride medium. Influences of factors as ionic strength, presence of the complexing ligands are evaluated for each sorption medium. The sorption of mercuric hydroxocomplexes is supposed in correspondence with already found sorption of mercuric hydroxides on kaolinite [3] and on SiO_2 [4], both studied by means of batch techniques. Accumulation of soluble mercury hydroxide on silica was found on the silica modified carbon paste electrode, too [5].

The aim of the contribution is to find mercury species efficiently sorbed on the montmorillonite. Speciation of the metals in the sorption medium plays important role in their sorption on the clay particles in the aquatic system.

References

1. Kula P, Navrátilová Z, Kulová P, Kotouček M (1999) Anal. Chim. Acta 385:91 - 101
2. Navrátilová Z, Kula P, submitted to Fresenius J Anal Chem
3. Singh J et al.(1996) Clays and Clay Minerals 44: 41 - 48
4. Mac Naughton M G, James R O (1974) J. Colloid Interface Sci. 47: 431 - 440
5. Walcarius A (1999) Proc. of An Interantional Conference Modern Electroanalytical Methods,Seč, Czech Republic, Book of Abstracts, No. PO41.

INSECT-ANTENNA – FET JUNCTION FOR BIOCHEMICAL SENSING

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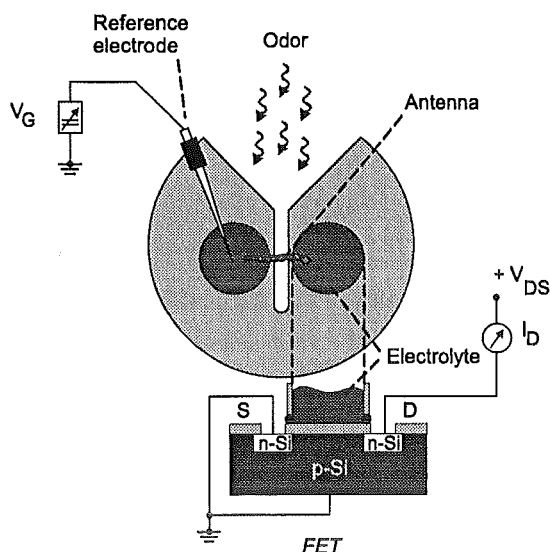
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Insect antennae are most suitable for the sensitive and selective detection of certain organic substances in air. In order to make these abilities usable in terms of analytical tools, a BioFET (biologically sensitive field-effect transistor) has been developed by establishing

a bioelectronic interface between the antenna of a potato beetle (*Leptinotarsa decemlineata* Say) and a FET (see figure). This biosensor is able to detect the “green-leaf odor” Z-3-hexen-1-ol in concentrations down to the low ppb range. Using this BioFET and a specially designed sensor system, measurements in a glasshouse were performed under real-world conditions. It could be shown that single damaged potato plants – liberating this kind of green-leaf odor – could be detected. This is

valuable for applications in agriculture, where the amount of pesticides could be minimized by the presented sensor.

In general, further applications are emerging, for instance in food quality assessment or early fire warning. Since many kinds of antennae may be employed for this type of BioFET, a huge number of substances is detectable. For future developments, it might also be possible to build up artificial antennae by identifying the respective receptor proteins and integrating them directly to the gate of a FET.



EFFECT OF Ca^{2+} ON THE ELECTROCHEMICAL DETECTION OF NADH WITH NITRO-FLUORENONE MODIFIED ELECTRODES

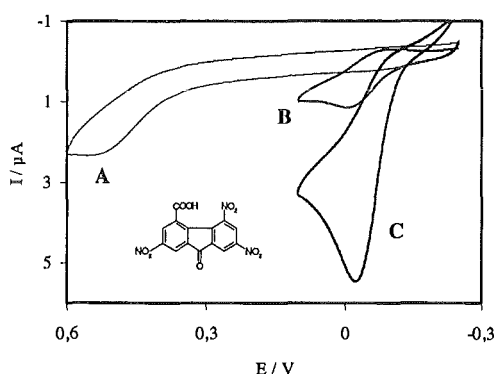
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Nitro-fluorenone derivatives are presented as a new family of redox mediators for NADH oxidation. Stable monolayers of these catalyst precursors are fixed on carbon, gold and platinum electrodes and are transformed electrochemically into the corresponding hydroxylamine compounds ($\text{R-NO}_2 + 4\text{e} + 4\text{H}^+ \Rightarrow \text{R-NHOH} + \text{H}_2\text{O}$). The subsequent reversible two electron oxidation of the hydroxylamine leads to the nitroso compounds ($\text{R-NHOH} \rightleftharpoons \text{R-NO} + 2\text{e} + 2\text{H}^+$) which exhibit high catalytic activity in the electrooxidation of NADH at very low overpotentials. Thus an efficient detection of NADH over a wide linear concentration range is achieved ($5\mu\text{M}$ - 2mM).

A dramatic increase (up to 500%) of the electrochemical signal is observed after addition of calcium ions to the solution. This is due to a bridging complexation of the coenzyme's phosphate groups with a carboxy group of the mediator via Ca^{2+} . The electrostatic binding enhances the electron transfer efficiency and allows the elaboration of sensors for analytes like glucose with good detection characteristics.

Electrooxidation of 0,5mM NADH on glassy carbon: **A**) without modification **B**) electrode modified with a monolayer of 2,5,7-trinitro-4-carboxy-9-fluorenone (see inset) **C**) same electrode but after addition of Ca^{2+}



References

1. N.MANO, A.KUHN, *Electrochem. Comm.* 1 (1999) 497
2. N.MANO, A.KUHN, *J.Electroanal.Chem.* 477 (1999) 79

ELECTROCATALYTIC REDUCTION AND DETERMINATION OF DISSOLVED OXYGEN ON POLY-NILE BLUE MODIFIED ELECTRODE

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Dissolved oxygen (DO) in environmental water is an important parameter of environment quality. Its determination has been accomplished by several methods such as EPR, chemical and electrochemical methods. Electrochemical methods for DO determination included using an oxygen electrode or some chemically modified electrodes (CMEs). However, some of these methods are time-consuming or suffer from high limits of detection. Most of CMEs to be used for DO determination were prepared with iron or cobalt porphyrin or other complexes of cobalt (II). A nafion-methyl viologen CME has been developed for this purpose. In this work, we obtain a dissolved oxygen sensor based on poly-nile blue modified glassy carbon electrodes (PNBE), which are prepared by electrochemical cyclic sweep between -0.6 and $+1.0$ V (vs.SCE) at 50 mV/s for 10 cycles in 0.1 M pH 6.3 PBS containing 0.5 mM nile blue.

With a continuous cyclic sweep the cyclic voltammogram of the PNBE in pH 6.3 PBS shows a pair of stable redox peaks. The peak-to-peak separation is about 139 mV at 50 mV/s. With increasing scan rate, the peak-to-peak separation increases and a charge transfer coefficient of 0.17 is obtained, the peak currents is proportional to the scan rate, displaying a surface controlled quasi-reversible process. The formal potential at pH 6.3 is -0.386 V calculated with the equation of $E^{o'} = E_{p,a} - \alpha(E_{p,a} - E_{p,c})$. From the slop of $E^{o'}$ vs pH, the electrode reaction of PNBE is a $2e$ and $2H^+$ process. The surface coverage of nile blue units in the polymer film is 1.39×10^{-10} mol/cm².

The PNBE shows an excellent electrocatalytic ability to DO reduction at pH 4.8 - 5.5. The reduction peak current of nile blue unit increases for 5 times. The catalytic peak current is proportional to DO concentration in the range of 3.2 to 18 ppm. A water sample is analyzed at 23°C for DO content by the PNBE method and a classic iodimetry. The obtained DO concentration is 8.7 ppm and 9.1 ppm, respectively, giving a small relative deviation of -4.6% .

This study is supported by the National Natural Science Foundation of China (No. 29975013 and 29835110).

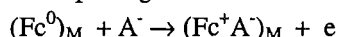
**ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE RESPONSE TO
POLY(VINYLFERROCENE) FILM REDOX DOPING BY
HEXAFLUOROPHOSPHATE; HEXAFLUOROARSENATE AND
HEXAFLUOROANTIMONATE ANIONS**

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Redox switching of the poly(vinylferrocene) (PVF) film in 0.1 M sodium hexafluorophosphate, hexafluoroarsenate, hexafluoroantimonate solutions has been investigated. The redox conversion of immobilized ferrocene (Fc^0)_M to ferricenium cation (Fc^+)_M and simultaneous ion-pairing of the latter with the counter anion (A) /1/



has been studied using cyclic voltammetry (CV) and potential-step Electrochemical Quartz Crystal Microbalance (EQCM) /2/.

The EQCM allowed both counter anion and water transfers into/out of the PVF film due to electrochemical perturbation (CV or potential-step) of the system to be studied. Water partition into the PVF film has been calculated from the difference in the gain in mass detected by the EQCM and that found from the coulometry data.

The choice of the doping anions allowed the ion-pairing between ferricenium cations and counter anions upon oxidation of the PVF film to be studied by a gradual increase in both the size and the mass of the anions with the same composition (XF_6^- ; where X = P, As or Sb) and the structure (octahedral symmetry).

The PVF film demonstrates the ability of "electrochemical recognition" of the doping anions employed as found from the CV measurements. The current peak potentials in cyclic voltammograms of the PVF film were shifted to more positive potentials with the increase in the size of the counter anions. However, the redox switching kinetics of the PVF film was faster in hexafluoroantimonate solution compared to hexafluoro-hphosphate and hexafluoroarsenate as evidenced from the CV and the potential-step data.

The partition of water into the PVF film upon its oxidation increased with the increase in the size of the counter anion. The water entries were delayed compared to the counter anion transfers as found from the potential-step EQCM data. The stoichiometry and the kinetics of the redox switching of the PVF film are discussed in terms of the ion-pair formation, anion and water transfers into/out of the film and the possible structural changes that may occur in the polymer /3/.

References

1. S. Bruckenstein, P. Krtil and A.R. Hillman, J. Phys. Chem. B, 102 (1998) 4994.
2. S. Bruckenstein and M. Shay, J. Electroanal. Chem., 188 (1985) 131.
3. S. Bruckenstein and A.R. Hillman, J. Phys. Chem. B, 102 (1998) 10826.

Acknowledgments: financial support from the NSF (CHE-9616641) is greatly acknowledged.

REAGENTLESS GLUCOSE BIOSENSORS. EVIDENCE FOR ELECTRON-HOPPING VIA POLYMER-BOUND OS-COMPLEXES IN AN ELECTROCHEMICALLY DEPOSITED REDOX POLYMER

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„Wiring“ of redox proteins aiming on reagentless biosensors has received increasing interest over the past decade [1,2]. However, manual deposition of the used redox hydrogels limited this approach with respect to mass production and rational control of the electrode architecture. Simultaneously, electrochemical deposition of conducting-polymer films with concomitant entrapment of redox enzymes has led to biosensors which can be in principle produced avoiding any manual procedure [3,4]. In order to combine advantages seen in the use of electron-transfer cascades by means of electron-hopping between polymer-bound redox relays and the non-manual electrochemical deposition of conducting-polymer films, the development of redox-relay modified conducting-polymer films have been proposed [5].

In this communication, a reagentless glucose biosensor is presented, in which glucose oxidase is entrapped in a pyrrole/Os-complex-functionalized pyrrole/copolymer during the electrochemical-induced polymerisation process. To prove the envisaged electron-hopping process via adjacent Os-relays at the conducting-polymer backbone rigorous exclusion of molecular oxygen is necessary to avoid the side reaction via O_2 as electron acceptor. Due to the shift of the oxidation potential of H_2O_2 at glassy-carbon surfaces it could be shown that the current observed at an applied potential of 500 mV vs. Ag/AgCl is exclusively related to the proposed redox cascade via the polymer-bound Os-centres. Moreover, the electron-transfer pathway between the polymer-entrapped enzyme and the electrode surface is not impaired by oxygen present in the electrolyte solution.

Optimisation of the proposed reagentless biosensor architecture is performed by variation of the key parameters for the formation of the conducting co-polymer film, the modulation of the hydrophilicity of the conducting-polymer backbone, and the exchange of the counter anion of the Os-complex. Strategies for the design of an optimised molecular architecture as a prerequisite for improved electron-transfer pathways in reagentless amperometric biosensors will be discussed.

References

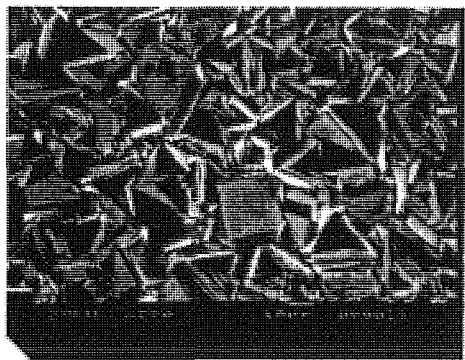
1. A. Heller, *Acc. Chem. Res.* **23** (1990) 128-33
2. A. Heller, *J. Phys. Chem.* **96** (1992) 3579-3587
3. N.C. Foulds, C.R. Lowe, *J. Chem. Soc. Faraday Trans.* **82** (1986) 1259-1264
4. W. Schuhmann, *Mikrochim. Acta* **121** (1995) 1-29
5. W. Schuhmann, C. Kranz, J. Huber, H. Wohlschläger, *Synthetic Metals* **61** (1993) 31-35

ELECTROANALYSIS AT BORON-DOPED DIAMOND ELECTRODES

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Boron-doped diamond with a doping level of 10^{19} to 10^{20} cm⁻³ is a new and versatile electrode material [1] with high electrical conductivity and unusual chemical and physical



properties. The diamond electrodes can be grown in form of thin polycrystalline films on tungsten substrates (see Figure) via a chemical vapour deposition procedure, or obtained commercially in form of free-standing plates. The surface of the crystalline diamond undergoes chemical changes in the course of redox cycling at positive or negative potential [2], during treatment with plasma [2], or after exposure to an electron beam [2].

Both metal deposition at negative potentials and metal oxide deposition at positive potentials can be employed for analytical accumulation procedures at boron-doped diamond electrodes [3,4]. A rapid 'mercury-free' cathodic stripping voltammetry (CSV) procedure based on the accumulation of PbO₂ on an oxidised diamond electrode in the presence of power ultrasound [3] has been developed with high sensitivity (10^{-8} M) and low interference from other elements.

- [1] Yu. Y. Pleskov, Russ. Chem. Rev., 68, 1999, 381.
- [2] For a review see C.H. Goeting, F. Marken, A. Gutierrez-Sosa, R.G. Compton, J.S. Foord, New Diamond and Frontier Carbon Technol., 9, 1999, 207.
- [3] A.J. Saterlay, C. Agra-Gutierrez, M.P. Taylor, F. Marken, R.G. Compton, Electroanalysis, 11, 1999, 1083.
- [4] A.J. Saterlay, F. Marken, J.S. Foord, R.G. Compton, in preparation.

CHEMICALLY MODIFIED ELECTRODES WITH DNA AND CYCLODEXTRIN

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The formation of adducts of various low molecular mass analytes with deoxyribonucleic acid and cyclodextrins is known in analytical chemistry and it has found also an application at the electrochemical sensors. Voltammetric electrodes chemically modified with these host macromolecules allow to recognize and preconcentrate some groups of the trace analytes such as drugs and risk chemicals of a suitable structure before their electrochemical quantification. In this work, the carbon paste electrode, glassy carbon electrode and carbon based screen-printed electrodes were modified by calf thymus double stranded DNA and β -cyclodextrin as well as its polymer using the adsorption of the modifier from solution (dip coating or solvent evaporation techniques) and the attachment in polymeric films.

Cyclic voltammetry, differential pulse voltammetry and potentiometric stripping analysis were used for the electrochemical measurement of the accumulated electroactive analyte itself, the redox marker competing with a non-electroactive analyte at the association with the host macromolecule and the changes in the signal of the DNA guanine-residue due to the association with the analyte. Simple, fast and sensitive analytical procedures were proposed for the determination of the azepine, phenothiazine, acridine, catechin, quinazoline, pyrene derivatives and phenolic antioxidants. The detection limits down to nM concentrations were found.

The results obtained with the electrochemical sensors were validated by the fluorimetric measurement with a thiazole orange derivative TO-PRO-3. The formation of inclusion complexes for polymeric cyclodextrins was studied by the combination of voltammetric and piezoelectric techniques. The values of the association constants were obtained.

The application of the electrochemical sensors described here for an investigation and elucidation of the interaction of DNA with drugs, chemicals and their reaction products is of great environmental and medical interest. The DNA modified electrodes were used at the detection of damage to DNA. The effect of inhibitors on changes in the DNA structure was also tested.

NEW GLUCOSE BIOSENSORS BASED ON PRUSSIAN BLUE AND CRYSTALLINE, CROSS-LINKED AND LYOPHILIZED GLUCOSE OXIDASES: A COMPARATIVE STUDY

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Prussian Blue (PB) was found to be a selective electrocatalyst of H₂O₂ reduction at – 50 mV vs. Ag/AgCl [1]. Low potential of peroxide detection allows to provide a high selectivity of analysis in the presense of interferences. Potentiostatic deposition of PB on glassy carbon electrode and enzyme immobilization resulted in biosensor preparation. Nafion[®] (perfluorinated sulfonate ionomer) was used for glucose oxidase (GOx) immobilization. Two GOx immobilization methods which were developed earlier were used in this study: (i) deposition of layer of enzyme aqueous solution followed by covering with layers of Nafion[®] solution in ethanol; (ii) deposition of GOx-Nafion[®] mixture in 90% ethanol [2].

The aim of this work was to compare new glucose oxidase preparations, crystals and cross-linked enzyme crystals (CLEC[®]s) (CLEC[®] is registered trademark of Altus Biologics Inc., 625 Putnam Ave, Cambridge, MA 02139, USA) with commercially available lyophilized GOx (Sigma) in terms of biosensor characteristics. The best performance was obtained for biosensor based on powdered GOx CLEC[®]. In this case, the linear range of glucose flow-injection analysis (FIA) was from 2.5 μ to 2.5 mM, detection limit of 2.5 μ M and sensitivity of 20 μ A cm⁻² mM⁻¹. The latter value was several times higher, then for biosensors based on crystal (Altus) and lyophilized (Sigma) GOxs. The operational stability of both CLEC[®] and lyophilized GOx based sensors was 100 % during 7 hours of continuous FIA.

The influence of interfering species in concentrations corresponding to the upper therapeutic limit in blood was tested. Acetaminophen (0.15 mM) and urate (0.5 mM) caused a very low anodic response, ascorbate (0.1 mM) had no response. In the presense of interferences response to glucose (1 mM) suffered a slight decrease of ca. 2 %.

[1] A. A. Karyakin, O.V.Gitelmaher, E. E. Karyakina. Anal. Chem., 67 (1996), 2419.

[2] A. A. Karyakin, E. E. Karyakina, L. Gorton, O. A. Bobrova, L. V. Lukachova, A. K. Gladilin, A. V. Levashov. Anal. Chem. 68 (1996) 4335

HIGHLY SELECTIVE AMPEROMETRIC GLUCOSE BIOSENSOR BASED ON CARBON PASTE MODIFIED WITH COPPER AND GLUCOSE OXIDASE

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In the last years the development of glucose amperometric biosensors using glucose oxidase (GOx) as recognition layer has received considerable attention. In the case of bioelectrodes based on glucose quantification from the hydrogen peroxide enzymatically generated, different methodologies have been used to circumvent the problem of the high overvoltage necessary for the anodic or cathodic determination.

The goal of this communication is to present an amperometric glucose biosensor based on the incorporation of copper microparticles and GOx into a matrix of carbon paste. It is known that copper offers a strong electrocatalytic action towards the reduction of hydrogen peroxide. However, this effect is not preferential for peroxide species because copper also catalyzes the oxidation of ascorbic and uric acids. Taking into account these aspects, the amount of copper in the paste was regulated in order to get the best compromise between sensitivity and selectivity.

An important decrease in the overvoltage for the reduction of hydrogen peroxide was obtained allowing to select -0.100 V as working potential. The bioelectrode was challenged with uric and ascorbic acids up to 5.0×10^{-4} M and 2.83×10^{-3} M, respectively, and no interference was observed even for such high concentrations. Human blood serum samples, obtained from Hospital Nacional de Clínicas (Cordoba National University) were used to study the matrix effect and to evaluate the applicability of the bioelectrode to these complex real samples. Glucose determinations in samples of known glucose concentration (obtained by the classic spectrophotometric enzymatic method) were performed with this bioelectrode and the results showed errors of around 5 %.

The bioelectrode presented here has proved to be very useful for the fast, sensitive and highly selective glucose determination without using artificial redox mediators or selective membranes.

CELL BIOSENSORS ABLE TO OPERATE IN ORGANIC SOLVENT OR GASEOUS MEDIUM FOR THE ANALYSIS OF BENZENE, PRELIMINARY RESULTS

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In recently years the authors of this communication fabricated an electrochemical biosensor based on *Pseudomonas putida* cells, immobilised in an agarized culture medium, for the purpose of determining traces of benzene, working in aqueous solution, using a classical gaseous diffusion amperometric oxygen electrode as transducer [1]. After performing a complete electroanalytical characterisation of the biosensor, the response to traces of benzene and several benzene derivatives was evaluated in water. As our group developed in the last years several biosensors able to operate directly in n-hexane [2,3], actually we are studying the possibility of operating in n-hexane solutions in which benzene and its derivatives are of course more soluble. In the last year Bachman et al. described a similar biosensor, but for the analysis of benzoic acid and phenol [4]. At this moment the problem is represented by the low reproducibility of our biosensor working in organic solution, due to the difficulty of standardise the cell growth and the immobilisation of the *Pseudomonas Putida*, but we have already demonstrated the possibility to develop such kind of biosensor; at this end, we already characterised the response of this probe increasing the benzene concentration working in n-hexane solution and evaluated its sensitivity and its linearity range. Although the obtained results are not completely satisfying the efforts go on with the aim of reaching the construction of a biosensor for the control of benzene in fuels.

Better results were obtained using a similar biosensor to evaluate the benzene concentration in air; really, lower values than that one indicated by the current law as "quality objective", can be determined even if our preliminary tests were performed by an experimental apparatus simulating the urban city's air.

References

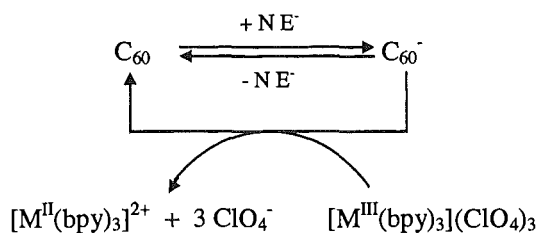
1. L.Campanella, G. Crescentini, M.G. D'Onorio, M.Tomassetti, *Ann. Chim.*, **86** (1996) 527
2. L. Campanella, G. Favero, M.P. Sammartino, M. Tomassetti, *Talanta*, **46** (1998) 595
3. L. Campanella, U. Martini, M.P. Sammartino, M.Tomassetti, *Electroanalysis*, **8** (1996) 1150
4. T.T. Bachmann, U. Bilitewski, R.D. Schmid, *Anal. Lett.*, **31** (1998) 2361

ELECTROCATALYTIC REDUCTION OF FULLERENE C₆₀ AT ELECTRODES MODIFIED BY [M^{III}(BIPIRIDINE)₃](ClO₄)₃ (M = CO AND FE)

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In media of low dielectric constant containing tetra(*n*-butyl)ammonium perchlorate as a supporting electrolyte oxidation of [M^{II}(bpy)₃]²⁺ leads to the precipitation of solid electrochemically inactive phase of [M^{III}(bpy)₃](ClO₄)₃ on the electrode surface. In the presence of fullerene in solution electrodes modified by his solid phase are shown to display catalytic wave that results from chemical reduction of the film by C₆₀^{•-} according to the scheme:



The catalytic current associated with the reduction of C₆₀ at a modified electrode can be used for the quantitative determination of fullerene concentration in solution. The reduction current associated with square wave voltammetric experiments increased linearly with the concentration of C₆₀ in the range of 0.25-20 μM. Electrodes modified with [Co^{III}(bpy)₃](ClO₄)₃ exhibit better analytical performance than those covered by [Fe^{III}(bpy)₃](ClO₄)₃. Ultramicroelectrodes modified with [Co^{III}(bpy)₃](ClO₄)₃ were used to quantify the fullerene concentration in flow injection analysis. In proposed analytical procedure the solution containing both [Co^{II}(bpy)₃]²⁺ complex and determined C₆₀ fullerene was injected to the flow stream of acetonitrile/toluene (1:4, v/v) mixture containing (*n*-Bu)₄NClO₄. The triangular potential waveform was applied to the gold electrode. During the positively-going potential scan the electrode was covered by electrochemically inactive [Co^{III}(bpy)₃](ClO₄)₃ layer. In cathodic cycle the catalytic current of C₆₀ reduction was recorded. A linear dependence between current signal of catalytic C₆₀ reduction and fullerene concentration was observed in a concentration range from 5×10⁻⁷ to 2×10⁻⁵ M. Although the method is addressed to quantify fullerenes it could be easily adopted to other compounds with formal potential more negative than the potential of [Co^{II}(bpy)₃]²⁺ oxidation.

VOLTAMMETRIC DETERMINATION ON MODIFIED ELECTRODES OF ACTIVE PRINCIPLES IN DRUGS

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The determination of the active principle in a drug is a very meaningful step as the efficiency of the drug as well as its possible toxicity are strictly depending on the active principle concentration.

In this paper we propose the voltammetric determination of four different principles used in commercially available drugs.

The analysis was performed by cyclic voltammetry using modified working electrodes (glassy carbon, Au, Pt on which conducting polyaniline was electrochemically deposited comparing the results with those ones by different pulse polarography (DDP), a much more common technique applied to pharmaceutical field analytical problems.

In ethanol solution we obtained a signal due to polyaniline and affected by the analysed principle concentration to which it can be inversely correlated. The detection limit resulted to the $5 \cdot 10^{-7}$ mol/L against $5 \cdot 10^{-5}$ mol/L of DPP with a linearity range of two and half decades ($5 \cdot 10^{-7}$ - 10^{-5} mol/L). The method resulted to be rapid cheap, reproducible and accurate.

Finally usnic acid, one of the four principles investigated, hypothesised as detoxifying agent versus heavy metals, was studied in the system cadmium ions/cysteine with reference to the possible complexation of the metal by cysteine with masking of a very important radical scavenger of human organism and successive release of cysteine due to the reaction between metal ions and usnic acid.

IRIDIUM-DISPERSED ENZYMATIC CARBON PASTE ELECTRODE FOR THE QUANTIFICATION OF PHENOLS AND CATECHOLS

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In the last decade there has been great interest in the development of biosensors. The electrochemical biosensors, especially enzymatic ones, based on the combination of the high specificity of biocatalytic processes with the advantages of the electrochemical transduction, have proved to be very useful for the quantification of different metabolites.

In the present communication an amperometric bioelectrode for the quantification of phenols and catechols of clinical, pharmacological and environmental interest, based on the incorporation of iridium microparticles and polyphenol oxidase (PPO) within carbon paste matrices, is described.

The determinations were performed amperometrically in 0.050 M phosphate buffer (pH 7.40) at -0.100 V as this potential allows us to obtain the best compromise signal-to-noise. Commercial enzyme and fresh banana tissue were employed for the measurements. The studied compounds were phenol, L-tyrosine, acetaminophen, catechol, L-dopa and dopamine.

The effect of iridium and PPO content in the paste on the response of the bioelectrode is evaluated. The iridium-doped carbon paste electrode displays excellent electrocatalytic activity towards the reduction of the enzymatically formed quinone species. Thus, the quantification of the micromolar/submicromolar levels of phenols and catechols can be performed at potentials lower than in the case of bare CPE with much better sensitivity (around 4-fold higher). The analytical performance as well as the kinetic parameters for the different substrates, is evaluated.

DIRECT MODIFICATION OF ZINC ELECTRODE WITH ZINC HEXACYANOFERRATE FILM

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The studies of direct modification of many metal hexacyanoferrate films modified electrodes have been reported [1-3]. In the present study direct modification of zinc electrode with zinc hexacyanoferrate film was studied and the electrochemical behavior of the constructed electrode was investigated. The direct modification process or chemical formation of a thin layer of zinc hexacyanoferrate film on the surface of a zinc electrode was carried out by dipping the zinc electrode into a potassium hexacyanoferrate(III) solution containing 0.1 M KCl as supporting electrolyte for a certain time which control the film thickness. The effects of the concentration and pH of modifier solution on the electrochemical behavior of the direct modified electrode were investigated. The film formed on the electrode surface was stable and insoluble in both organic and aqueous solutions. This novel electrode has many preferences in addition of modified electrodes due to its ease of construction, simplicity of using, low resistance and *etc.* Electrocatalytic activity of the modified electrode was investigated towards some typical compounds such as ascorbic acid and hydrogen peroxide. Electrochemical behavior and properties of the mentioned electrode were compared with an indirect zinc hexacyanoferrate film modified electrode [4]. The experimental results show that this novel modified electrode could be prepared simply and it has good stability and a long useful life. This type of electrode modification can be used as a very useful method for preparation of modified electrodes for various applications.

References

1. A. Eftekhari, *Electrochem'99*, Portsmouth, UK, 1-3 September, 1999.
2. A. Eftekhari, *9th I S on Heterogeneous Catalysis*, Varna, Bulgaria, 23-27 September, 2000.
3. A. Eftekhari, submitted to *197th ECS Meeting*, Toronto, Canada, May 19-24, 2000.
4. A. Eftekhari, submitted.

TWO STRATEGIES WITH THIRD GENERATION ORGANIC CONDUCTING SALT BASED ENZYMATIC BIOSENSORS : ELECTROPOLYMERIZATION OVER THE SALT AND ITS ENTRAPMENT INTO A SOL-GEL MATRIX

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Organic conducting salts (OCS) electrodes are widely used in third generation amperometric enzymatic biosensors owing to its conductivity and the ability of mediate the re-oxidation of the flavin centre of redox enzymes or NAD(P)H dependent dehydrogenases, without the need of other additional artificial electron-transfer mediator. In particular, the TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) salt is one of the more popular for this purpose.

In this work an *in situ* polymerization method allows the electrosynthesis of polypyrrole conducting films (PPy) and the non-conducting poly(*o*-phenylenediamine) (oPPD) in a flow system by using as electrode substrate an organic conducting salt of TTF-TCNQ. The enzyme glucose oxidase (GOx) is previously immobilized into the organic salt cross-linked with glutaraldehyde, and then a polymeric bilayer was fabricated by cyclic voltammetry from +0.10 to +0.65 mV. at a scan rate of 25 mV/s. Owing to the partial decomposition of the salt with high anodic potentials (above +0.40 V approximately) or cathodic (about less than 0.10 V), care should be taken in exposing the sensor at these potentials when the electropolymerization is carried out. The procedure allows to obtain a selective biosensor for glucose determination.

In the another approach, a sol-gel matrix is used for immobilizing the GOx enzyme and the TTF-TCNQ salt. The OCS is incorporated into the sol-gel material by mixing with the starting sol-gel solution; previously, the enzyme solution is mixed with the salt. An efficient conductivity for this electrode material and good charge-transfer mediation is obtained by the doping of the sol-gel material with this salt, as seen when the glucose oxidase is re-oxidized and the currents obtained. The analytical performance of the two above mentioned approaches in the glucose determination is presented and compared.

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**GOLD ELECTRODES MODIFIED WITH NEW PHENOTHIAZINE
DERIVATIVE: ELECTROCHEMISTRY AND ELECTROCATALYTIC
OXIDATION OF NADH**

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Phenothiazine derivatives are suitable mediators for electrocatalytic oxidation of NADH [1], whose efficient and reversible recycling is of particular interest for the construction of dehydrogenase based amperometric biosensors [2], fine chemicals industry using NAD⁺ dependent biocatalists [3] and for energy conversion *via* biofuel cell [4].

The electrochemical behavior of a phenothiazine derivative, 18H-dibenzo[c1]-7,9-dithia-16,18-diazapentacene (DDH), spontaneously adsorbed on gold electrode surface, has been studied. The investigated adsorbate-adsorbent couple was selected taking into account the nature and intensity of interactions involved in the obtaining of self-assembled nanostructures.

From cyclic voltammetry measurements, performed in aqueous buffer solutions at different potential scan rates and pH values, the rate constant of the heterogeneous electron transfer and transfer coefficient were estimated. Cyclic voltammograms shapes, the linear dependence between the peak current and the potential scan rates pointed out a quasi-reversible, surface confined redox process. Considerable values for surface coverage, some specific evolution of voltammetric signal and the studied molecule nature lead to the supposition about the existence of an organized nanostructure of DDH on gold surface.

Some preliminary studies confirm that the investigated compound, adsorbed on the gold surface, exhibit electrocatalytic activity toward NADH oxidation. The electrocatalytical efficiency was evaluated from cyclic voltammetry measurements .

References

- [1] L.Gorton, J.Chem. Faraday Trans. I, 82 (1986) 1245.
- [2] I. Katakis and E. Domínguez, Micrichim. Acta, 126 (1997) 11.
- [3] S.Itoh, M.Kinugawa, N.Mita and Y.Oshiro, J.Chem.Soc., Chem.Comm., (1989), 694
- [4] G.T.R. Palmore, H. Bertschy, S.H. Bergens and G.M. Whitesides, J. Electroanal. Chem., 443 (1998) 155

MERCURIC-GRAPHITE MODIFIED ELECTRODES IN VOLTAMMETRICAL HEAVY METALS DETERMINATION

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The search for deviation reason between the signal and the ideal value is motivated by high sensitivity of mercuric-carbon electrode (MCE) 'in situ' mode, and insufficient regeneration of its surface.

The experiments were performed on P-5827M potentiostat with a three-electrode arrangement. Rotating carbon disk electrode (RCDE) was used as a working electrode, rotation of which was provided only on accumulation phase. The electrode was made from pyrolytic graphite impregnated by paraffin and polyethylene under vacuum. Modified carbon electrodes were made from spectral graphite with implantation of insoluble mercury salts: Hg_2Cl_2 , $\text{Hg}_2(\text{SCN})_2$, mercury-ethylene diamine (EDA) compound. Silicone was used for providing contact in cells. Analysis was done with 1M HCl. The ions under study were Cu^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} with addition of third element Ge for pair Cu-Zn. Mercury ions concentration in solution was 10^{-5} mol/l in comparison to defined ions concentration of $10^{-7} - 10^{-8}$ mol/l.

'In situ' mode with usage of RCDE analytical signal (AS) value was indicated to be dependent on prehistory of carbon electrode, i.e. terms of usage, elements nature (which were deposited during that period), electrode surface regeneration mode – mechanical or electrochemical. Assumption to implantate mercury into graphite structure was proved by emissive spectrum analysis by means of lines blackening. In 20 cathode-anode cycles with 20s delay when $E = -1,3$ V, electrode surface was mechanically and electrochemically regenerated, and then graphite was examined to detect metal presence. Pure graphite was taken for comparison. It was observed that Cd, Pb and Zn content was equal in both samples, although Hg and Cu contents were three times different. This reason was the basis for making electrodes that were modified by mercury compounds. In this case it was unnecessary to add Hg^{2+} to the solution.

Cyclic and stripping voltammetry helps to study mercury discharge ionization processes at all modified electrodes, to define electrochemical parameters, particularly number of electrons, which participate in reduction-oxidation. It was found, that electrode processes include chemical reaction phase if RCDE is 'in situ' mode and the electrode is modified by Hg_2Cl_2 .

Mercuric-graphite structure of modified electrodes considerably reduces systematic errors in determining heavy metals ions in potable and industrial waste water. Electrode modified by ethylene diamine complex of mercury has the highest AS regeneration. Accuracy of the results during natural water analysis was proved by methods of atomic-absorption spectroscopy.

APPLICATION OF KINETIC DATA FOR OPTIMIZATION OF ELECTROCHEMICAL IMMUNOASSAY

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Various methods of electrochemical immunoassay and particularly electrochemical enzyme immunosensors are very promising for solving different problems of analytical chemistry. Analytical abilities of enzyme immunosensors could be extended due to investigation of influence of various factors on catalytic activity of enzymes, which used as a label in different methods of immunoassay. Selection of experimental conditions which allow to observe maximal analytical signal is very important to due its possibility to improve sensitivity and selectivity. Application of cholinesterase (ChE) as a label allows to control passage of immunological reaction and to determine various compounds which could affect to the ChE activity. It was established that interaction of some antigens (Ag) with the corresponding antibodies (Ab) influenced on ChE activity and immune complex formed acted as effector (inhibitor or activator) for the enzyme. Experimental conditions for determination of Ag pathogenic fungi *Trichophyton rubrum* (TR) with amperometric enzyme immunosensor were selected using kinetic data. Dependencies of enzyme reaction passage on pH of solution, Ab dilution and concentrations of substrate (Cs) and Ag (C_{Ag}) were investigated. Kinetic parameters (K_m and V_{max}) for various pH (8.0-10.05) and Cs (5×10^{-4} - 2×10^{-3} M) were calculated. Under the experimental conditions immune complex acts as activator of ChE and type of activation is related to combination of all factors; in the most cases pseudoactivation or two-inconcordant activation were observed. It was experimentally established that effect of pH on ChE activity prevailed over its influence on immunological reaction and maximal analytical signal under pH 9.05 $\pm$ 0.1 was observed. Application of Cs 2×10^{-3} , 1.5×10^{-3} and 1×10^{-3} M has some advantages in every case but results obtained with Cs 5×10^{-4} M were less suitable for immunosensor operation. Thus, kinetic data allowed to select experimental conditions: 1:20 Ab dilution, pH 9.05 $\pm$ 0.1 and Cs 1 - 2×10^{-3} M; which gave possibility to determine Ag TR with amperometric enzyme immunosensor in concentration range 1×10^{-5} - 8×10^{-6} mg/ml.

**ELECTROCHEMICAL CATALYTIC REDUCTION OF DIOXYGEN BY
COBALT(II) HEMATOPORPHYRIN COMPLEX IMMOBILIZED ON SILICA
GEL INCORPORATED IN CARBON-PASTE ELECTRODE**

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Many papers have reported the electrocatalysis for oxygen reduction at metalloporphyrin modified electrodes. In most cases, the porphyrins containing meso substituents catalyze only the reduction of O_2 to H_2O_2 , while the direct reduction of O_2 to H_2O is catalyzed by dimeric complexes containing porphyrins without substituents in the meso positions.

In this work we report the electrochemical properties of the complex formed by Co(II) with hematoporphyrin (ligand without meso substituents), previously immobilized on silica gel, incorporated into a carbon-paste electrode. The supported complex is monomeric and catalyzes the four-electron reduction of O_2 to H_2O (measured at a rotating-disk electrode). The catalytic rate constant of the dioxygen with the cobalt-hematoporphyrin catalyst was estimated as $k_{O_2} = 2.6 \times 10^6 \text{ mol}^{-1} \text{ l s}^{-1}$, being larger than the values presented for not supported dimeric catalysts. For the calculation of diffusion-convection limited currents (I_L) at rotating-disk electrode by Levich equation, $I_L = 0.620nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C_{O_2}$, the following parameters were employed: diffusional coefficient, $D = 7.5 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ (obtained by Cottrell equation); kinematic viscosity of aqueous solutions, $\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$; concentration of O_2 , $C_{O_2} = 0.88 \text{ mol l}^{-1}$; the Faraday constant, $F = 9.648 \times 10^4 \text{ A s mol}^{-1}$ and the electrode area, $A = 0.5 \text{ cm}^2$. The total quantity of cobalt on the electrode surface was equal to $5.7 \times 10^{-6} \text{ mol cm}^{-2}$. The influence of pH was studied in the range 2.0 to 8.0 using 0.5 mol l^{-1} KCl solution as supporting electrolyte and does not indicate a significant change in the formal potential values.

SOFT DRINKS SUCROSE DETERMINATION USING A MICROBIAL BIOSENSOR BASED ON OXYGEN ELECTRODE WITH ELECTROLYTE IN NON-AQUEOUS MEDIUM

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Sucrose biosensors are usually realised using a three enzymes system¹ involved in a sequence of enzymatic reactions catalysed by invertase, mutarotase and glucose oxidase. Direct determination of sucrose in glucose - containing samples was achieved using a multilayer enzyme electrode². Instead of isolated enzyme, yeast cell walls were utilised as an invertase source in a hybrid sucrose biosensor³.

Use of intact yeast cells of *S. cerevisiae* on the surface of an oxygen electrode represents an alternative to the enzymatic biosensor for sucrose⁴. Selectivity of this sensor is assured by using a second glucose oxidase and catalase layer. To decrease the level of detected concentrations and to enlarge the calibration range was used an oxygen electrode based on electrolyte in non-aqueous medium (LiCl in ethanol)⁵.

In order to optimise the yeast concentration in the biocatalytical layer there were tested different microbial membrane (absorbance at 660 nm between 0.05 – 0.4). Optimum cell concentration corresponds to an absorbance at 660 nm of 0.1.

Response time for the microbial biosensor prepared with an acetyl cellulose membrane with immobilised yeast cells was approximately 2 min. Optimum conditions were temperature 30 °C and pH 5. Microbial biosensor respond in the range of 10^{-5} – $3 \cdot 10^{-3}$ M sucrose (steady-state method).

Using a second enzymatic layer based on GOD and CAT, the interference of glucose in determination of sucrose decrease from 15% to maximum 4%. This hybrid biosensor was used to determine sucrose concentration in soft drinks. Results have been compared with spectrometric method with dinitrosalicylic acid and showed a good correlation.

References

1. Satoh, I., Karube, I., and Suzuki, S., *Biotechnol. Bioeng.*, **1976**, 18, 269.
2. Scheller, F., and Renneberg, *Anal. Chim. Acta*, **1983**, 152, 265.
3. A. Barlikova, J. Svorc, and S. Miertus, *Anal. Chim. Acta*, **1991**, 247, 83.
4. L. Rotariu, C. Bala, S. Fleschin, and V. Magearu, *Roum. Biotechn. Lett.*, **1996**, 1, 47.
5. V. Magearu and A. Ciucu, *Anal. Lett.*, **1990**, 23(11), 2005.

SENSOR FOR HYDROGEN PEROXIDE BASED ON PRUSSIAN BLUE MODIFIED ELECTRODE: IMPROVEMENT OF THE OPERATIONAL STABILITY

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Improvement of the operational stability of amperometric sensor based on Prussian Blue (PB) modified glassy carbon electrode is presented. The long term performance of the sensor was evaluated by injection of hydrogen peroxide (5 μM in potassium buffer) solutions in a flow-injection system during 5-10 h. The following parameters and correlated with the performance of the sensor were investigated; the times for electrodeposition and electrochemical activation, temperature, storage time, pH, composition of the buffer solution and sample injected volume. As analytical characteristics of the modified electrode can be emphasized: initial sensitivity of $0.3 \text{ A cm}^{-2} \text{ M}^{-1}$, detection limit of *ca.* 0.5 μM , precise results (r.s.d. < 1.5%) and possibility to carry out around 50 samples (50 μL) per hour.

Keywords: Stability; Prussian Blue; Hydrogen peroxide; Flow-amperometry

ELECTROCHEMICAL PROPERTIES OF MIXED IRON/COBALT HEXACYANOFERRATE FILM MODIFIED ELECTRODE

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Preparation of bilayered metals hexacyanoferrate film modified electrodes have been reported [1]. Kulesza et al. [2] reported hybrid metal nickel/cobalt hexacyanoferrate film. More recently [3,4] we described the electrochemical properties of electrodes modified with mixture of metals hexacyanoferrate film. A modified electrode with mixture of iron and cobalt hexacyanoferrates film was fabricated and its electrochemical behavior and electrocatalytic properties were investigated. Modification of the electrode surface was carried out by electrodeposition of a thin mixture film of iron and cobalt on a graphite electrode and chemical transformation of the deposited mixture film to hexacyanoferrate salts was done by dipping the deposited electrode into a $K_3Fe(CN)_6$ solution containing 0.1 M KCl as supporting electrolyte. The electrocatalytic activity of the modified electrode towards electrochemical oxidation of hydrogen peroxide was investigated. The analytical applicability of the mixed iron and cobalt hexacyanoferrate film modified electrode as an amperometric sensor for the determination of hydrogen peroxide was studied. Several modified electrodes were constructed with various ratios of the iron and cobalt hexacyanoferrate film which were controlled by the concentration of the first modifier solution. The electrochemical response of the different electrodes were compared.

References

1. A. Dostal, M. Hermes, F. Scholz, *J. Electroanal. Chem.*, 1996, **415**, 133.
2. P. J. Kulesza, *et al.*, *J. Electrochem. Soc.*, 1999, **146**, 3757.
3. A. Eftekhari, submitted to *51st ISE Meeting*, Warsaw, Poland, 3-8 September, 2000.
4. A. Eftekhari, submitted to *8th IM on Chemical Sensors*, Basil, Switzerland, 3-5 July, 2000

AN APPLICATION OF CHOLINESTERASE AMPEROMETRIC BIOSENSOR IN ENVIRONMENT MONITORING OF SIM-1,3,5-TRIAZINE HERBICIDES CONTAMINATION

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A worldwide usage of agricultural chemicals can result in an environment pollution by their residues. The sim-1,3,5-triazines represent a large group of herbicides used in many parts of the world. Owing to their persistence in soil they can be found in surface, drinking waters and food. Thus a development of sensitive, rapid and reliable methods of determination of these substances is very important for protection of the environment and human health. A variant of immunochemical analysis of s-triazine herbicides (simazine, atrazine and propazine) using amperometric immunoenzyme systems was developed. This variant consists of several steps which include an extraction of one of triazine herbicide using immobilized antibodies (Ab) against it, followed by a detection of this triazine herbicide concentration by amperometric cholinesterase biosensor (AChB). The application of immunoreaction Ab-antigen makes this variant of analysis selective, and the electrochemical detection using AChB is advantageous among others as more rapid, simple and sensitive method. The working conditions of immunochemical determination of sim-1,3,5-triazine herbicides were defined. The optimal concentration of substrate for determination of simazine, atrazine and propazine were chosen as 8×10^{-4} M, 2×10^{-3} M and 5×10^{-4} M correspondingly; CAb for immobilization were defined for simazine as 9.7 mg/ml and for atrazine as 16.4 mg/ml. Under the chosen conditions the immunochemical determinations of simazine and atrazine in water samples were carried out. The dynamic ranges of concentration were for simazine 5×10^{-11} - 1×10^{-8} M, $C_{lim} = 5 \times 10^{-12}$ M and for atrazine 1×10^{-11} - 1×10^{-7} M, $C_{lim} = 5 \times 10^{-12}$ M.

The study has been carried out under financial support of the INCO Copernicus grant #ERBIC15-6698-0910.

REAGENTLESS BIOSENSORS BASED ON SELF-DEPOSITED $\text{Fe}_4(\text{PMO}_9)_2$ FOR GLUCOSE AMPEROMETRIC DETECTION

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Continuing our research on the mediated electroreduction of H_2O_2 at modified electrodes [1-2] and taking into account the interesting electrocatalytic properties of polyoxometallates [3-4], a self-assembling technique was used for the amperometric detection of glucose [5-6].

A basic structure has been obtained using a layer-by-layer self-deposited architecture, built-up on electrostatic interactions on gold electrodes and containing: 3-mercaptopropylsulfonic acid (MPS) negative monolayer followed by a B (Binder) layer, a POM negative layer and a new positive B layer: where Binder represents a positively-charged poly(vinylpyridine) based polymer and POM is a heteropolymolybdate complex $\text{Na}_{10}[\text{Fe}_4(\text{PMO}_9\text{O}_{34})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ [$\text{Fe}_4(\text{PMO}_9)_2$], respectively. The Au/MPS/B/POM/B structure was used as electrochemical interface to connect to electrode a glucoseoxidase negatively charged layer and to obtain a reagentless amperometric biosensor.

All investigated multi-layer structures were characterized by cyclic voltammetry, performed in the potential range of -0.4 to +0.6 V/Ag/AgCl, KCl_{sat} , in a 0.4 M Na_2SO_4 solution, pH = 6, at different potential scan rates (5, 10, 25 and 100 mV/s).

Analytical parameters (stability and kinetic constants) of the electrode confirm the obtaining of an efficient transducer using a versatile enzyme immobilization technique with good characteristics.

References

- [1] I. C. Popescu, S. Cosnier and P. Labbe, *Electroanalysis*, 9 (1997) 998.
- [2] S. Gaspar, L. Muresan, A. Patrut and I. C. Popescu, *Anal. Chim. Acta*, 385 (1999) 111.
- [3] K. K. Shiu and F. C. Anson, *J. Electroanal. Chem.*, 309 (1991) 115.
- [4] C. Sun, J. Zao, H. Xu, Y. Sun, X. Zhang and J. Shen, *J. Electroanal. Chem.*, 435 (1997) 63.
- [5] J.J. Gooding, D.B. Hibbert, *Trends Anal Life Sci*, 1, 1997, 1-12
- [6] L. Cheng, S. Dong, *Electrochem. Commun*, 1 (1999), 159.

ELECTROCATALYTIC ACTIVITY OF CARBON PASTE ELECTRODE MODIFIED WITH OSMIUM IN CHOLINESTERASE ENZYME SYSTEMS

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The properties and application field of biosensors depend greatly on the way of analytical signal registration. Among electrochemical biosensors, potentiometric and amperometric detectors are widely used. The response of amperometric biosensor is based on electrochemical activity of the substrates or products of enzyme interaction on the different electrodes. That's why the application of chemically modified electrode (CME) based on the electron transfers is very perspective. As known cholinesterase catalyzes hydrolysis reaction of thiocholine ethers for example butyrylthiocholine iodide (BTCI) or butyrylthiocholine chloride (BTCCl): $RC(O)SCH_2CH_2N(CH_3)_3X + H_2O \rightarrow RCOOH + HSCH_2CH_2N(CH_3)_3X$, $R=C_3H_7$, $X=I, Cl$.

Electrochemical activity of the hydrolysis product - thiocholine was used for substrate determination. Electrochemical signal observed in the mixture after enzyme interaction on the carbon paste electrode at $E \sim 0.60$ V corresponds to thiol oxidation. Immobilization of spongy osmium as a redox-mediators in electrode composition leads to electrocatalytic response registration during thiol oxidation. The voltammograms obtained on CME in borate buffer solution (pH=8-9) show step at $E \sim 0.70$ V corresponding to electron transfer $Os(III) \rightarrow$

$Os(IV)$. The height of this signal increases significantly in the presence of thiocholine. It is proposed that catalytically active species are surface-bond oxyosmium groups which mediate thiol oxidation via heterogeneous redox catalysis. Electrode modified by spongy osmium was used as amperometric detector in flow analysis of thiocholine ethers. The calibration plots for BTCI and BTCCl at hydrodynamic conditions (flowing rate $u = 4.0$ ml/min) are linear in the range $1 \times 10^{-3} - 1 \times 10^{-6}$ mol/L. Replicates of the electrocatalytic signal yield a relative standard deviation of current response less than 3 %. CME based on spongy osmium exhibits excellent electrocatalytic stability in the flowing stream.

ELECTROCHEMICAL PROPERTIES OF MIXED IRON/COBALT HEXACYANOFERRATE FILM MODIFIED ELECTRODE

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Preparation of bilayered metals hexacyanoferrate film modified electrodes have been reported [1]. Kulesza et al. [2] reported hybrid metal nickel/cobalt hexacyanoferrate film. More recently [3,4] we described the electrochemical properties of electrodes modified with mixture of metals hexacyanoferrate film. A modified electrode with mixture of iron and cobalt hexacyanoferrates film was fabricated and its electrochemical behavior and electrocatalytic properties were investigated. Modification of the electrode surface was carried out by electrodeposition of a thin mixture film of iron and cobalt on a graphite electrode and chemical transformation of the deposited mixture film to hexacyanoferrate salts was done by dipping the deposited electrode into a $K_3Fe(CN)_6$ solution containing 0.1 M KCl as supporting electrolyte. The electrocatalytic activity of the modified electrode towards electrochemical oxidation of hydrogen peroxide was investigated. The analytical applicability of the mixed iron and cobalt hexacyanoferrate film modified electrode as an amperometric sensor for the determination of hydrogen peroxide was studied. Several modified electrodes were constructed with various ratios of the iron and cobalt hexacyanoferrate film which were controlled by the concentration of the first modifier solution. The electrochemical response of the different electrodes were compared.

References

1. A. Dostal, M. Hermes, F. Scholz, *J. Electroanal. Chem.*, 1996, **415**, 133.
2. P. J. Kulesza, et al., *J. Electrochem. Soc.*, 1999, **146**, 3757.
3. A. Eftekhari, submitted to *51st ISE Meeting*, Warsaw, Poland, 3-8 September, 2000.
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VOLTAMMETRIC DETERMINATION OF DNA EFFECTORS USING DNA BASED BIOSENSOR

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The development of new sensitive and highly selective electrochemical biosensors for analytical control of medical and environmental objects is one of the most important problems of chemistry. Enzyme biosensors and sensors based on immunological reactions have been used in this area. At the same time the biosensors based on DNA have found only limited application, whilst these devices can serve as a new tool for pharmacological and ecological monitoring. DNA molecules are very sensitive to the presence of various metal complexes, medicines and environmental contaminants which effect or damage the structure of the molecules. The combination of active DNA indicator layer with an electrochemical transducer allows one to use both high sensitivity of biological reactions and the advantages of this method of detection for the investigation of the mechanism of DNA-metal complex interaction and evaluation of the toxicity of various compounds. The amperometric biosensor was developed based on stationary Hg-film electrode and cellulose nitrate film containing molecules of denatured DNA for the determination of effectors of DNA such as Pt(II) and Pt(IV) complexes as anticancer agents. Pt(II) and Pt(IV) content was monitored by the height of the corresponding cathodic peaks observed at -0,9 and -1,2 V vs. s.c.e., these signals being hydrogen catalytic liberation waves produced due to immobilized DNA complexing with Pt. The detection limit for Pt(IV) is 1.0×10^{-10} mol/l, for Pt(II) - 1.0×10^{-10} mol/l. The determination of cis-dichlorodiamino platinum in blood serum was performed ($7-0.3 \times 10^{-6}$ mol/l, $\text{rsd} < 0.02$). The toxic effect of heavy metals to DNA and possibility of environmental control was studied using Cd(II) as an example. The peak current at -0,65 V was decreased due to Cd(II) complexing with DNA. This effect is proportional to Cd(II) concentration up to 1.0×10^{-7} mol/l. Cd(II) was determined in natural water with the biosensor and the determination data were compared with the ones obtained by atomic-absorption spectrometry. The reactivation procedure was developed.

Poster Contributions

Session D

ELECTROCHEMICAL DETERMINATION OF TRACE METALS IN ECOTOXICOLOGICAL TESTING

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The toxicity of chemical species is often evaluated through ecotoxicological tests on model organisms. For trace metals, the organism employed is usually *Daphnia magna*. In the inorganic "hard water" ASTM medium to which are added vitamins, an algae extract and the food for the *Daphnia*, which is *Selenastrum capricornutum*. It is of interest to explore the correlation between the toxicity of the metal ions in the organisms, measured through acute and chronic tests, and the values determined electrochemically.

Thus, electrochemical determination of lead and cadmium ions has been carried out in the ASTM medium in the absence and in the presence of one or more of the additives to evaluate how these influence the level of labile metal ion in solution. The batch injection analysis (BIA) technique was employed, together with anodic stripping voltammetry at Nafion-coated mercury film electrodes.

There is an influence from each of the components on the observed concentrations. The organic extract causes a decrease in the signal, the vitamins an increase. Studies have been carried out with concentrations used in chronic tests, up to $150 \mu\text{g l}^{-1} \text{Pb}^{2+}$ and $5 \mu\text{g l}^{-1} \text{Cd}^{2+}$. Experiments have been carried out with living organisms over a 4-day period. Our results show some correlation between toxicity, measured as fertility and rate of growth, and the different concentrations of trace metal ion measured electrochemically.

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**DAILY QUALITY ASSURANCE BY ELECTROANALYTICAL
DETERMINATION OF TRACE ELEMENTS IN ENVIRONMENTAL SAMPLES**

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Stringent quality assurance and harmonisation of protocols for each step of the analytical procedures are fundamental requirements for long-term environmental monitoring. Electroanalytical techniques like potentiometric stripping analysis and different modes of stripping voltammetry were used for trace element determinations in liquid and solid samples of different origin. To minimize possible matrix effects (e.g. presence of organic compounds in the solution used for the measurement) procedures for the determination of Se, Cd, Pb, Zn, Ni, Co, Pt and Rh were developed which are based on high pressure digestion with nitric acid. The following quality assurance steps were developed and incorporated into these procedures:

- use of in-house (matrix identical) reference material and certified reference material in each digestion series,
- intermethod comparisons by using other methods,
- participation in interlaboratory comparison exercises,
- participation in certification campaigns for candidate reference materials from international and national organisations.

Selected results for each of these steps will be presented and discussed.

**THE INDIRECT INVERSVOLTAMMETRIC DETERMINATION OF THE
BISMUTH COMPLEX FORMATION CAPACITY IN WINE - A METHOD TO
ESTIMATE IRON CLOUDINGS IN WINE**

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Metal cloudings in wine appear uncontrollably in barrel or bottles and can not be eliminated except by the so called „Blauschönung“. The most unpleasant and economically fatal ones are the cloudings caused by iron (, copper and aluminium) especially if they appear when the wine is already bought by the consumer. The reason for the iron cloudings is the oxidation of iron(II) to iron(III) catalysed by copper. In contrast to iron(II) iron(III) forms disturbing cloudings of ironhydroxides, ironphosphates including organic substances like tannins or proteins. Not all wines have a tendency to form iron cloudings. Iron cloudings are dependent on the iron concentration in wine and the concentration of strong chelating (organic) agents. While the total iron concentration in wines can be determined by AAS or ICP-OES no simple method to determine the sum of strong chelating agents is available at present.

A method for the determination of the sum of strong bismuth chelating agents in ground and drinking water was adopted to the matrix wine. The differential pulse inverse voltammetry is a very sensitive method for the determination of bismuth in very low concentrations. The use of this method allowed to determine bismuth chelating agents in the sub ppb range. Therefore the wines were diluted 10-fold with ultra pure water. A solution of ascorbic acid and potassiumchlorid, adjusted to pH=1, and bismuth is added to the sample. After 1 h of reaction time, which is necessary to transfer the chelating agents into the bismuth chelates, the free bismuth can be determined by standard addition after accumulation on a hanging mercury drop electrode at -125 mV (against Ag/AgCl) and the total bismuth in the same way after accumulation at -1000 mV. The difference of both results gives the strongly bound bismuth. The calculated difference of the added bismuth and the total bismuth determined inversvoltammetrically after accumulation at -1000 mV gives the bismuth which is very strong bound to chelating agents. In addition to this kinetic experiments could be done. Therefore the time dependent peak highs of free and total bismuth are measured.

The aim of the new method in combination with iron determination by AAS or ICP-OES is to detect the potential of iron clouding in wine very early and to stabilise the wine by wine making methods. A great advantage for the wine practitioner.

RESOLUTION OF VOLTAMMETRIC OVERLAPPED PEAKS USING CHEMOMETRICS MULTIVARIATE CALIBRATION METHODS

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Multivariate calibration methods have become an important tool in analytical chemistry. The great advantage of these methods is enable to extract quantitative information from non-specific data, avoiding the need of previous separation step [1-3].

In this work two multivariate calibration methods, Partial Least Squares (PLS) and Principal Component Regression (PCR) were used to resolve overlapping voltammograms obtained in the analysis of solutions containing Cd(II), Tl(I), Pb(II) and In(III) by differential pulse anodic stripping voltammetry.

The calibration matrix was designed according to a factorial experimental design consisting of 2^n plus a central point, resulting 17 quaternary mixtures. Another 6 mixtures were randomly prepared and used as test set.

Internal validation was performed using a cross validation method, leaving out one sample at a time, in order to select the optimal number of factors to be used to build the calibration models for each metal ions.

The effect of using either voltammograms or first derivative voltammograms in the quality of calibration and prediction will be discussed and the predictive ability of the calibration models will be compared.

References:

- [1] H. Martens, T. Naes, *Multivariate Calibration*, Wiley, Chichester, 1989.
- [2] M. C. Antunes, J. E. J. Simão, A. C. Duarte, *Port. Electrochim. Acta*, 1996, 14, 189-192.
- [3] M. C. Antunes, J. E. J. Simão, A. C. Duarte, *Port. Electrochim. Acta*, 1997, 15, 345-349.

DETERMINATION OF HETEROGENEOUS COMPLEXATION PARAMETERS THROUGH VOLTAMMETRIC TECHNIQUES

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Voltammetric methods are frequently used for heavy metal speciation studies in natural waters [1]. It has been shown that adsorption effects are greatly minimised, for labile complexes, using limiting currents from Reverse Pulse Polarography [2]. We are now tackling the difficulty arising from the fact that the macromolecule often contains sites with different affinities for the metal ion (heterogeneity) [3-5].

The rigorous numerical simulation of this problem [6,7] indicates that limiting currents for homogeneous complexation are a good estimation for the currents in heterogeneous systems with the same bulk concentration values [8]. An approximate analytical solution relating the current to the free metal concentration in the bulk solution has been suggested for a wider use of the voltammetric techniques [8].

The accuracy of the approximated expression is tested for complexation models involving discrete affinity spectra (two kinds of sites) or continuous affinity spectra (gaussian distribution of log k). As the approximate expression is straightforwardly inverted, it allows the computation of the whole binding curve from normalised limiting current data corresponding to a suitable series of titrations of fixed amounts of ligand with metal.

References

- [1] J.Buffle, Complexation Reactions in Aquatic Systems. An Analytical Approach., Ellis Horwood Limited, Chichester, 1988, Chapter 9, p. 467.
- [2] J.Galceran, D.Rene et al. *J. Electroanal. Chem.* 375 (1994) 307.
- [3] H.P.vanLeeuwen and J.Buffle, *J. Electroanal. Chem.* 296 (1990) 359.
- [4] M.Filella, J.Buffle and H.P.vanLeeuwen, *Anal. Chim. Acta* 232 (1990) 209.
- [5] J.P.Pinheiro, A.M.Mota and M.L.S.S.Gonçalves, *J. Electroanal. Chem.* 402 (1996) 47.
- [6] J.Galceran, J.Cecilia et al., *J. Electroanal. Chem.* 472 (1999) 42.
- [7] J.Puy, M.Torrent et al., *J. Electroanal. Chem.* 457 (1998) 229.
- [8] J.L.Garces, F.Mas et al. *J. Electroanal. Chem.* In press .

SEQUENTIAL-INJECTION STRIPPING ANALYSIS (SISA) OF NIFUROXIME USING DNA-MODIFIED GLASSY CARBON ELECTRODES

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Previously, it has been shown that DNA-modified electrodes can be successfully used to analyse various drugs which are able to interact specifically with the DNA backbone [1,2]. Potential-induced preconcentration of the drug on the surface of the modified electrode followed by stripping voltammetry has been used to quantify these drugs. However, until now, this technique had been predominantly applied in stationary polarographic cells. Problems concerning electrode regeneration by means of potential cycling had been encountered, leading to a limited long-term stability of the modified electrodes. Very recently, we have investigated possibilities to adapt stripping voltammetry to a sequential-injection analyser. Sequential injection stripping analysis (SISA) of traces of mercury using modified could be successfully demonstrated [3].

Here, we report on the development of an analytical method for the determination of nifuroxime (5-nitro-2-furancarboxaldehyde oxime) using SISA and stationary stripping voltammetry. For this, the voltammetric behaviour of nifuroxime was investigated using cyclic voltammetry and differential pulse voltammetry at bare and DNA-modified glassy-carbon (GC) electrodes, which were obtained by adsorption of dsDNA on the glassy-carbon surface followed by hybridisation of ssDNA. In cyclic voltammetry reduction of nifuroxime at DNA-modified electrodes gives rise to a well-defined peak, and in contrast with bare GC surfaces, a re-oxidation peak could be observed.

Optimisation of the preconcentration process at the DNA-modified surface led to a significant enhancement of the voltammetric current response, a better defined peak shape and an improved dynamic range. Based on this optimised voltammetric procedure, SISA has been evaluated for the determination of nifuroxime. The flow-system significantly facilitates the regeneration of the DNA-modified electrode surface, hence diminishing problems related to accumulation and memory effects. The linear detection range could be extended to 65 μM with a detection limit (3σ) of 0.68 μM , which corresponds to an absolute amount of 21 ng nifuroxime. Results concerning the determination of nifuroxime at DNA-modified electrodes using SISA will be presented.

References

- [1] E. Palecek. *Electroanalysis* 8 (1996) 7-14.
- [2] A.M. Oliveira Brett, S.H.P. Serrano, I. Gutz, M.A. La-Scalea, M.L. Cruz. *Electroanalysis* 9 (1997) 1132-1137.
- [3] I. Turyan, T. Erichsen, W. Schuhmann, D. Mandler. *Electroanalysis*. submitted.

MULTIVARIATE CURVE RESOLUTION AS A TOOL FOR THE INTERPRETATION OF OVERLAPPING VOLTAMMETRIC SIGNALS

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Extracting analytical information from voltammetric signals is usually a matter of fitting the parameters of a previously assumed model to a series of limiting or peak currents and half-wave or peak potentials. This strategy is known as Hard Modelling and for the (especially interesting) case of metal complexes is based in models such as those by Lingane, DeFord-Hume or Schaap-McMasters [1]. For relatively simple signals, Hard Modelling provides excellent results. However, the presence of overlapping signals and/or secondary phenomena such as electrodic adsorption can seriously affect its applicability. In these cases, an alternative strategy can be used which is termed Soft Modelling and is based on multivariate curve resolution (MCR) analysis by means of an alternating least squares (ALS) optimization [2].

In contrast with Hard Modelling, MCR-ALS Soft Modelling does not impose any model for the electrochemical processes. Instead, it determines concentrations and pure signals for every electroactive species just by analysis of signal variation at different metal-to-ligand ratios. The only hypothesis which is made is the linearity of the signals with respect to the concentration, which is true (or close to be true) in many kinds of electrochemical systems. Although it was originally developed for spectrophotometric data [2], the MCR-ALS method has shown interesting possibilities in the analysis of voltammetric signals [3].

In this work, the MCR-ALS method is applied to the interpretation of two data sets which are especially intricate: some cyclic voltammograms (CV) of the system Cd(II) + glutathione (with electrodic adsorption and overlapping of many signals) and some differential pulse polarograms (DPP) of the system Cu(II) + tannic acid (which, in addition to the problems above, is also affected by the formation of intermediate species of Cu(I)).

References

1. Crow, D.R. (1969) *Polarography of Metal Complexes*, Academic Press, London.
2. Tauler, R.; Smilde, A. and Kowalski, B.R. (1995) *J. Chemometrics* 9, 31-58.
3. M. Esteban, C. Ariño, J.M. Díaz-Cruz, M.S. Díaz-Cruz and R. Tauler, (2000) *Trends Anal. Chem.*, 19, 49.

**DETERMINATION OF HEAVY METALS IN FISH MUSCLE TISSUE BY
DIFFERENTIAL PULSED ANODIC STRIPPING VOLTAMMETRY**

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Heavy metals (Cu, Zn, Cd, Pb) were determined in fish muscle tissue samples originating from two fish species (Brown trout *Salmo trutta m. fario*, Grayling *Thymalus thymalus*) from two rivers (Topľa, Slaná) from the east part of Slovakia. After decomposition of fish muscle tissue by dry ashing we determined the contents of particular heavy metals by differential pulsed anodic stripping voltammetry. The obtained experimental values of contents were discussed in relation to the following aspects: hygienic quality of meat, place of catching, period of catching and fish age group. The heavy metal content in fish muscle tissue is a reliable criterion for monitoring the heavy metal pollution of aquatic ecosystems, taking into account the real complexity of the problem.

ELEMENT TRACES AND ULTRATRACES IN WINE

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Experience by the determination of Pb, Cd, and Cu in wine by potentiometric stripping analysis (PSA) have demonstrated that these low cost method can be used for wine monitoring. In the last two centuries the copper concentration (about 0.25 µg/ml) in wine not change significantly. In these time the cadmium concentration reduced from 4 ng/ml to 0.3 ng/ml and lead from 30 µg/ml to 30 ng/ml. Anodic stripping voltammetry was used for thallium and bismuth determinations. The concentrations found in not polluted areas were 0.1-0.2 ng/ml for both elements. In areas with industrial activities an elevated values were found in the plants but not in the wine. Platinum concentrations in wine determined by adsorptive stripping voltammetry were 0.5-1 pg/ml and not change in the last 50 years.

**DETERMINATION OF IODIDE IN TABLE SALTS CONTAINING SOME
ANTICAKING AGENTS USING STRIPPING POTENTIOMETRY WITH
SELECTIVE
SENSING AT A TRICRESYL PHOSPHATE-BASED CARBON PASTE
ELECTRODE**

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Since ion chromatography suffers high chloride background, standard photometric and titration methods are rather time consuming and lack on sensitivity, and the ICP-MS approach requires an expensive equipment, a new principle of electrochemical detection of iodide at a tricresyl-phosphate (TCP)-based carbon paste electrode (CPE) [1,2] seems very promising for iodide determination in table salts as it offers good sensitivity, selectivity and reliability, direct

measurement (no sample pretreatment except its dissolution in water), short analysis time (ca 5 min per sample), inexpensive instrumentation, and field measurements. In addition, when using stripping potentiometry, common anticaking additives to salts do not interfere.

A complete procedure for the determination of iodide in commercial table salts has been elaborated utilising constant current stripping potentiometry at a CPE containing TCP as a liquid binder. Due to a synergistic accumulation based on ion-pair formation combined with extraction mechanism [1], the method is extremely selective allowing to detect iodide in highly saline solutions and in the presence of some minor constituents such as $K_4[Fe(CN)_6]$ (food additive "E 536") and MgO added to salts as anticaking agents. With this procedure, the signal to iodide concentration was linear in the range of 1 to 50 mg/kg salt with a DL ($S/N=3$) of about 0.5 mg/kg, and a recovery rate of 90-110%. The proposed method has been applied to determine iodide in various commercial table salts and the results obtained ($RSD = \pm 9\%$) agreed with those found by a reference photometric method.

References

- [1] I. Švancara, J. Konvalina, K. Schachl, K. Kalcher, K. Vytras, *Electroanalysis* 10 (1998) 435
- [2] J. Konvalina, K. Vytras, *Electroanalysis* 10 (1998) 787

INVESTIGATION OF DEPOSITION AND STRIPPING PHENOMENA AT THE HEATED GOLD WIRE ELECTRODE IN COMPARISON TO THE ROTATING DISK ELECTRODE: COPPER(II), MERCURY(II) AND ARSENIC(III)

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In prior investigations concerning the positive effect of increased temperatures on stripping analysis the results of arsenic(V) and mercury(II) [1, 2] showed an improvement in the detection limit of up to 10 times. In the studies presented here, we intended to get more detailed information about the question how increased temperature acts on deposition and stripping steps.

Since the kinetics of reduction is fast for all three analytes, diffusion and/or convection should be rate determining. This was the reason to compare the results with that of rotating disk electrode. We were interested to answer the question whether the convection is responsible for increased transport, or whether the temperature dependence of the diffusion coefficient is the main reason.

The temperature effect on the stripping step itself was another problem to be studied. With solid electrodes, voltammetric stripping alone is insufficient generally to remove the deposited material completely. This problem was studied by application of three consecutive stripping scans following one deposition. With classic room temperature measurements at a rotating disk electrode, every scan resulted in a detectable signal. Signal amplitudes decreased in the ratio 3.6 : 1.4 : 1. With increased temperature during stripping, the material is removed from the surface much more efficiently, thus voltammetric signals of consecutive scans changed relatively in the ratio 18 : 1 : 1. Even if the heat is applied only during deposition there is a remarkable improvement of the signal ratio toward the prime scan (9.6 : 1.5 : 1). Probably, at a heated surface the material is deposited in a different form which can be oxidised more easily. It can be assumed that more and smaller nuclei are formed during deposition. There are more effects of temperature on deposition at metallic surfaces. So, e.g., an extremely enhanced diffusion process inside the electrode could change the electrode behaviour in undesired manner. To distinguish between such competitive processes, further investigation is in progress.

References

1. P. Gründler and G.-U. Flechsig, *Electrochim. Acta* **43** (1998) 3451
2. J. Wang, P. Gründler, G.-U. Flechsig, M. Jasinski, J. Lu, J. Wang, Z. Zhao, B. Tian, *Anal. Chim. Acta* **396** (1999) 33

VOLTAMMETRY OF GOLD COMPLEXES ON CARBON PASTE ELECTRODE

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Gold can be preconcentrated in form of its chlorocomplexes on the carbon paste electrode [1,2], chloraurate species were also sorbed on the glassy carbon electrode coated with poly(4-vinyl-pyridine) [3] and on the carbon fibers [4]. Anionic exchange of $[\text{AuCl}_4]^-$ was found on the carbon paste electrode modified with montmorillonite [5].

As Au(III) forms very strong complex with SCN^- anions, behaviour of the complex $[\text{AuSCN}_4]^-$ on the carbon paste electrode was studied, too. Although the SCN^- presence in the sorption chloride medium inhibited the open circuit sorption of the tetrachloraurates, the different results were found by differential pulse voltammetry of Au(III) in 0.1 M KCl in the presence of small amounts of SCN^- . The anodic peak of Au(III) increased with increasing amount of SCN^- up to maximum value at molar concentrations ratios of $\text{SCN}^- : \text{Au} = 1 : 1$ in the case of the montmorillonite modified electrode. The current can be enhanced by deposition at the potential -0.9 V. The limit of determination is supposed to be on the concentration level 10^{-7} mol/l Au(III) .

Using 0.1 M KSCN as the background electrolyte, the formation of $\text{Au} - \text{SCN}$ complexes was studied for the determination of gold in the gold sodium thiomalate (monogold(1+) sodium salt of mercaptobutanedioic acid) used as antirheumatic. The used voltammetric methods requires the preliminary oxidation of Au(I) bound on the thiomalate ligand [6] what results in complicated matrix for the subsequent voltammetry. The method in 0.1 M KSCN would enable to determine gold in such drugs by direct anodic DPV without sample pretreatment.

References

1. Kalcher K, Greschonig H, Pietsch R (1987) *Fresenius J Anal Chem* 327: 513-517
2. Vytras K, Švancara I, Renger F, Srey M, Varková R, Hvízdalová M (1993) *Coll Czech Chem Commun* 58: 2039-2046
3. Riley PJ, Wallace GG (1991) *Electroanalysis* 3: 191-195
4. Alarnes-Varela G, Gosta-García A (1997) *Electroanalysis* 9: 1262-1266
5. Z. Navrátilová, P. Kula, submitted to *Fresenius J Anal Chem*
6. G.M. Schmid, G.W. Bolger (1973) *Clin Chem* 19, 1002 – 1005

ELECTROCHEMICAL PROTEIN SEPARATION AND ELECTROCHEMICAL PROTEIN QUANTIFICATION METHOD

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A novel sensitive electrochemical method for the quantification of proteins is presented here. The assay is based on the biuret reaction, where copper ions form stable complexes with proteins in alkaline medium. In the present approach, once copper ions were complexed with the protein, they were released by an acidic treatment and simultaneously separated by ultra-centrifugation from the protein sample. This allowed to measure the released Cu^{2+} ions by Differential Pulse Anodic Stripping Voltammetry (DPASV) on Carbon Rotogravure Printed Electrodes (CARPEs) and directly relates Cu^{2+} concentration to the protein amount in the initial sample. A nM detection limit for Bovine Serum Albumin (BSA) was found with this method. The kinetic of this assay was tested and it resulted that the total assay can be carried out in 27 min, including incubation, washing steps and detection.

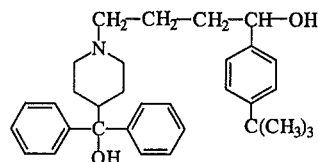
We shall also present a new method of protein separation based on Isoelectric Focusing in microchannels that allows the on-line purification of proteins in micro-total analysis systems.

DETERMINATION OF TERFENADINE IN ITS DOSAGE FORMS AND HUMAN SERUM BY ADSORPTIVE STRIPPING VOLTAMMETRY

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Terfenadine (I) is an electro-inactive pharmaceutical compound, hence it exhibits no direct response with different electrochemical techniques.



(I)

Controlled adsorptive accumulation of Terfenadine on the hanging mercury drop electrode (HMDE) in presence of Zn(II) provides the basis for direct differential pulse stripping voltammetry (DPSV) measurements at nanomolar concentration. Accumulation of Terfenadine in presence of Zn(II) was found to be optimized in 0.1M sodium perchlorate solution as supporting electrolyte under the following instrumental conditions: accumulation potential, -0.5V; accumulation time, 360 sec; scan rate, 5 mV/s and pulse amplitude 100 mV. Under these conditions the developed peak current of Zn(II)-Terfenadine complex adsorbed at the mercury electrode surface showed a linear dependence with concentration of Terfenadine in the range of $6 \times 10^{-8} - 9 \times 10^{-7} \text{ mol l}^{-1}$. The results obtained were found to be in good agreement with those obtained by HPLC method reported in the literature. The proposed method was successfully applied for determination of Terfenadine in its dosage forms and also in human serum. The average recoveries of Terfenadine were $98.85\% \pm 0.59$, $99.80\% \pm 0.397$ and $100.18\% \pm 1.27$ in its pure form, dosage forms and human serum, respectively with detection limit of 1.8 ng/ml Terfenadine.

INDIRECT VOLTAMMETRIC DETERMINATION OF QUATERNARY NITROGENOUS COMPOUNDS

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The quaternary nitrogenous – ammonium and pyridinium – compounds are used as medicaments and surfactants. Indirect determinations of these compounds obviously consist in extraction of its suitable ion-pair associates (1 : 1) from a water into an organic phase. Frequently used counter ions are picrate and azo-dye Orange II [1,2]. Quantification of the equivalent amount of the counter ion is proved by spectrophotometry or voltammetry. For instance, cetyltrimethylammonium bromide was determined voltammetrically as picric acid [3,4], cetyltrimethylpyridinium chloride, dodecyltrimethylammonium bromide etc. were determined by FIA as Fe-SCN-surfactant complexes with spectrophotometric detection [5].

In the present paper possibilities of the indirect voltammetric determinations of the representative ammonium and pyridinium bases were examined. The extraction conditions of the ion-pair associates with picrate and Orange II from the water to the chloroform phase were studied. A process of a dissolution of the extracted associates in the background electrolytes as well as the conditions of the voltammetric measurement were studied. Differential pulse voltammetry on HMDE was used.

The detection limits of proposed voltammetric determinations – in order 10^{-6} to 10^{-7} mol/l – are comparable with classical spectrophotometric and FIA ones. An advantage of the voltammetric determination is in the relatively simple instrumentation.

References

1. Kulová D., Koula V., J. Gasparič, Čsl. farm. 39 (1990) 357.
2. Koula V., Kulová D., Gasparič J., Collect. Czech. Chem. Commun. 57 (1992) 2272.
3. Kulová P., Kotoucek M., Modern Electroanal. Methods, An Int. Conference, Sept 19-23, 1999, Seč, Czech Republic, Book of Abstracts, poster no. PO/58.
4. Kulová P., Kotoucek M., Proc. of the XXXIII-th symposium about detergents and tensides, Nov. 1-3, 1999, Seč, Czech Republic. University Pardubice 99-47, 1999, ISBN-80-7194-223-5, pp.103-113(in Czech)
5. Patel R., Patel K.S., Talanta 48(4)(1999)923-931

AN OSCILLATING AND RENEWING SILVER ELECTRODE FOR CADMIUM AND LEAD DETECTION IN DIFFERENTIAL PULSE STRIPPING VOLTAMMETRY

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Traditionally a hanging mercury drop has been used as a working electrode in various voltammetric techniques. Due to the concern about using mercury in environmental analyses a great part of the research today deals with finding new electrode materials that can substitute the mercury electrode.

In this paper an electrode system using a silver working electrode oscillated by using a loudspeaker together with a silver counter electrode and a silver/silver chloride/saturated silver chloride/saturated potassium chloride reference electrode has been investigated. This system has showed a very good response for lead as well as for cadmium in a 0.01 M HCl solution. All analyses were performed by differential pulse anodic stripping voltammetry. Also the presence of copper in the detection of lead and cadmium has been investigated. The results show that copper has an insignificant influence on the lead and the cadmium detection in standard addition analyses. Concentration down to 1 ppb has been detected for lead and cadmium. The electrode system can be used repeatedly over a long period of time without maintenance because a new silver film is replated prior to each scan.

The silver electrode has been oscillated with both triangular and sine sound waves. The result shows that the response is more sensitive with use of triangular waves compared to sine waves. However the reproducibility is better for the electrode oscillated with sine waves. Also a study of the oscillating frequency has been carried out. The result shows that the response is considerably higher when low frequencies typically in the range 40 to 80 Hz is used, compared to higher frequencies typically over 150 Hz. With frequencies above 200 Hz, the response is similar to a still solution.

Good sensitivity together with the simplicity of using this maintenance free oscillating electrode makes this system potentially attractive for use in online and field instruments.

CHARACTERISATION AND TESTING OF CARBON PASTE-BASED ELECTRODES FOR THEIR USE IN STRIPPING POTENTIOMETRY

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Stripping potentiometry has already been well established and proved to be particularly powerful, in comparison with stripping voltammetry, in analyses of e.g. environmental water samples with "difficult" matrices, as it is less susceptible to organic and other interfering components. However, along with generally employed metallic (mostly mercury) film electrodes, only a few attempts were made so far to introduce new types of electrodes, as for example that one containing a built-in electrochemically resetable oxidant [1]. Therefore, it was decided to investigate the possibilities for extending the range of working electrodes in stripping potentiometry to carbon paste-based electrodes.

The basic characterisation of three different types of carbon paste electrodes for their use in stripping potentiometry was carried out by means of specially proposed testing procedures [2] and by using various model analyte systems. Carbon paste electrodes containing either paraffin oil, silicone oil or tricresyl-phosphate pasting liquids were tested as supports for mercury- and gold films, and as substrates for electrolytic, adsorptive, ion-pair forming, and extractive accumulation. Selected applications in organic electroanalysis (e.g., measurements in organic solvent-containing media, monitoring of some irreversible electrochemical reactions) were also performed. The interpretation of the results and observations based on individual testing measurements allowed to evaluate and to formulate some general conclusions and trends. The possibilities and limitations of the examined carbon paste-based electrodes in both chemical and constant current stripping potentiometry are outlined and discussed.

References

- [1] G. Tavčar, B. Ogorevc, X. Cai, B. Pihlar, *Anal. Chim. Acta* 329 (1996) 239.
- [2] I. Švancara, K. Schachl, *Chem. Listy*, 93 (1999) 490.

CADMIUM AND LEAD DETERMINATION IN HERBAL DRUGS BY POTENTIOMETRIC STRIPPING ANALYSIS

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In the past few years, an increased interest in herbs seems to occur in parallel to the back-to-nature movement. Modern technologies used for herbal drugs preparation make it possible to offer a lot of water soluble powders used for tea preparation. At the same time the spectrum of offered herbal drugs increases significantly. The natural contents of trace elements in plants depend on the species and origin. In some cases a significant bioaccumulation of some elements in herbs was observed. The knowledge about the influence of the herbal drugs composition to the elements concentration in the extracts is very limited.

Potentiometric stripping analysis was used for the determination of Cd and Pb on mercury film electrodes in water extracts from different herbs and water soluble drugs without any sample preparation. Experimental parameters (e.g. sample size, extraction time, pH and temperature), which can change the element concentration in the solution have been studied. A comparison between water soluble parts and total amounts (high pressure digestion with nitric acid) of Cd and Pb in original samples has demonstrated that Cd tend more than Pb to be soluble in water. In water extracts from tea based on rose hip elevated concentrations of cadmium and lead were observed due to low pH resulting from the herb itself.

THE EFFECT OF ALKYL LENGTH ON THE ANALYTICAL SIGNAL OF MONOALKYLEETHERS OF BUTYLENE OXIDE - ETHYLENE OXIDE BLOCK COPOLYMERS IN ADSORPTIVE STRIPPING TENSAMMETRY

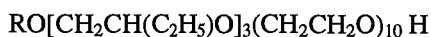
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In terms of application alkylalkoxylates are an increasingly important class of non-ionic surfactants. Monoalkylethers of butylene oxide - ethylene oxide block copolymers (ABE) [1] belong to this group. ABE are electroinactive and do not contain chromophoric groups. Therefore, the number of available analytical methods for ABE determination is very limited. Tensammetry provides an opportunity to increase the number of available analytical methods.

A series of four surfactants corresponding to the formula:



where R = n-C₁₀H₂₁ (C10), n-C₈H₁₇ (C8), n-C₆H₁₃ (C6) or n-C₄H₉ (C4), was investigated under the conditions of adsorptive stripping tensammetry (AdST). The morphology of tensammetric peaks, as well as peak height dependencies on the concentration of a corresponding surfactant, preconcentration time and potential were investigated. All four surfactants form negative tensammetric peaks roughly between -1.6 and -1.7 V. Peaks are mostly double or triple and only C4, C6 and C8 form single peaks for low concentration and short preconcentration time range. Peak height follow the sequence: C4 ~ C6 << C10 < C8. Calibration graphs show sigmoidal shapes in all instances and peak height dependencies vs. preconcentration time show a Γ- shape. Maximum peak height is obtained at a preconcentration potential of -0.2 V for C8 and C10, and at approximately -0.5 V for other cases. Anodic tensammetric curves show low value for analytical purposes.

Reference

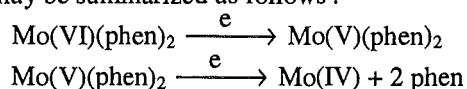
1. J.Chlebicki, J.Coll.Interf.Sci., 206(1998)77

A CATHODIC STRIPPING SQUARE WAVE VOLTAMMETRY OF THE MOLYBDENUM-1,10 PHENANTHROLINE COMPLEX

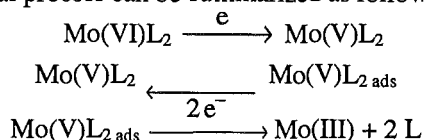
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The electrochemical behaviour of molybdenum in presence of phenanthroline by using various cathodic stripping voltammetric techniques was studied to elucidate the reduction mechanism of the Mo(VI)-phen complex. In a first part we examined the polarographic behaviour of Mo(VI) and Mo(V) in NaCl acidic medium in the absence and in the presence of phenanthroline. The electrode process of Mo(VI) in the presence of phenanthroline at the DME may be summarized as follows :



The results obtained at the HMDE by various electrochemical methods (ADPV, CV, ACP) show that the surface film is the result of the adsorption of the ligand and subsequent formation of a complex surface rather than the direct adsorption of the dissolved complex. The electrochemical process can be summarized as follows :



The adsorption in square wave voltammetry depends on the characteristics of the redox reaction. The current and the potential of the reduction are dependent on the frequency and the amplitude of the square wave signal and these parameters permit to characterise the nature of the redox process and to determine whether the reactant or the product (or the both) is/are adsorbed at the electrode. On the basis of the SW responses we have calculated the reaction parameters, i.e. transfer coefficient and maximum surface concentration and showed that the redox reaction of the adsorbed molybdenum complex is irreversible with the reactant adsorption.

**ELECTROCHEMICAL OXIDATION STUDY OF FENVALERATE AT A GLASSY
CARBON ELECTRODE.
A SQUARE WAVE VOLTAMMETRIC METHODOLOGY FOR ITS
DETERMINATION IN ENVIRONMENTAL WATER SAMPLES**

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Fenvalerate is a synthetic pyrethroid insecticide and is used to control a wide range of pests, including those resistant to organochlorine, organophosphorus, and carbamate insecticides. Uses include control of chewing, sucking, and boring insects in the wine culture. It is also used for insect control in homes and gardens and on cattle [1].

This work presents the electrochemical oxidation study of fenvalerate, in aqueous solutions, at a glassy carbon electrode. The oxidation reaction of fenvalerate did not occur directly at the electrode surface. A previous alkaline hydrolysis reaction was necessary, to obtain 3-phenoxybenzaldehyde, which is electrochemically active [2]. The oxidation of 3-phenoxybenzaldehyde was explored and a peak arose close to +1.5 V vs AgCl/Ag. Cyclic voltammetry was used to propose the irreversible oxidation mechanism of 3-phenoxybenzaldehyde at a glassy carbon electrode.

Based on the oxidation behavior of the pesticide an electroanalytical procedure was developed for the determination of fenvalerate in environmental samples. Preliminary studies showed that square wave voltammetry is the best technique suited to this purpose. The experimental conditions were optimised concerning pH, frequency, amplitude and step potential.

A calibration curve, obtained with five points, for a concentration interval of 4.8×10^{-6} – 2.4×10^{-5} mol/dm³ showed a straight line with $R = 1.0$. The limit of detection, calculated from the calibration curve [3], found was 7.9×10^{-7} mol/dm³.

The precision of the developed method was assessed by the relative standard deviation (RSD%), for ten consecutive determinations of standard solutions of 1.00×10^{-5} mol/dm³, and the value found was less than 0.4%.

Recoveries were determined to assess the accuracy of the results, The obtained values fluctuated between 95% and 108% and standard deviations between 2% and 5%.

References

- [1] The British Crop Protection Council, *The Pesticide Manual*, 11th ed., Surrey: The British Crop Protection Council, 1997, 539-541.
- [2] Corbini, G., Biondi, C., Proietti, D., *Analyst*, **118** (1993), 183-187.
- [3] Miller, J.N., *Analyst*, **116** (1991), 3.

**ANALYTICAL SIGNALS OF THE ION-PAIR TETRABUTYLAMMONIUM
CATION AND DODECYLBENZENESULPHNATE ANION IN ADSORPTIVE
STRIPPING TENSAMMETRY**

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Cationic surfactants (CS) are widely used as softeners and antistatic agents in laundering processes. In surface water CS are precipitated with anionic surfactants (AS); with the latter more in abundance. The behavior of CS and AS mixtures below a precipitation threshold is hardly studied. The aim of this work was an investigation of analytical signals of CS-AS ion-pairs in adsorptive stripping tensammetry (AdST) below a threshold of precipitation. A model system for investigation was a cationic tetrabutylammonium bromide (TBAB) and anionic sodium dodecylbenzenesulphonate (DBSNa) mixture. 1:1 mixtures of TBAB and DBSNa were investigated over a 50 nM – 2 mM concentration range i.e. up to precipitation threshold, under 120 seconds preconcentration conditions at a -0.70 V potential. Tensammetric curves show the formation of a single, wide well shaped tensammetric peak of the TBA-DBS ion-pair within the range of $0.1 - 1 \mu\text{M}$. Further increase in concentration causes a peak shift towards negative direction and a gradual transformation to a needleshaped peak. This is suggestive non-ionic surfactant behaviour [1,2].

Apart from the 1:1 mixtures, mixtures having an excess of one component (TBAB or DBSNa) were also investigated. Mixtures with very high DBSNa excess (of the order 100:1) show a strong response to TBAB concentration. Such a system may be used for TBAB indirect determination through changes in DBSNa peak height. Similarly, the mixtures with very high TBAB excess (two orders of magnitude) show a very strong response to DBSNa concentration and may be used for indirect DBSNa determination.

References:

1. A.Szymanski and Z.Lukaszewski, *Electroanalysis*, 3(1991)17
2. A.Szymanski and Z.Lukaszewski, *Electroanalysis*, 7(1995)114

VOLTAMETRIC DETERMINATION OF 6-BENZYLAMINOPURINE

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6-benzylaminopurine(BAP) represents one of cytokinins, natural plant growth regulators, widespread in plant micropropagation. We have developed new method for BAP quantification based on differential pulse voltametry (DPV) with mercury drop electrode. 0,05M-citric acid solution was found to be optimal for the quantification of tested compound with determination limit (DL) in submicromolar range (see Table I).

Table I. Voltametric determination of BAP

Method	concentration range [ng.ml ⁻¹]	Conditions	DL [ng.ml ⁻¹]
DPV on SMDE	11,3 – 28,7	0,05M-citric acid	7,88

Before DPV itself, the media for *in vitro* cultivation of plants containing BAP to be determined was preconcentrated by ion exchange chromatography, solid phase extraction and immunoaffinity chromatography. Described mode of DPV may become convenient method for monitoring of hormone consumption by plant with respect to the time of cultivation.

References

1. Pechová D.: Diploma Thesis. Palacký University, Faculty of Sciences, Olomouc 1999.

Acknowledgement

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STRIPPING ANALYSIS OF 3- METHYLYXANTHINE AND 7-METHYLYXANTHINE AT THE CHARGED INTERFACE

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The biological importance of 3- methylxanthine and 7-methylxanthine has stimulated our considerable interest in stripping analysis of these biological compounds. The elucidation of their interaction with the charged model interface mercury / aqueous electrolyte is significance for a critical evaluation of their adsorptive accumulation in stripping analysis. In this context cyclic voltammetry indicates the adsorption and association of these compounds and the effective interfacial accumulation of the Hg(II)-xanthate film on the electrode surface. The effective preconcentration associated with the adsorption of Cu(II)-xanthate complex on the HMDE results in a highly sensitive method for trace determination of these compounds in presence of Cu(II). Experimental and instrumental parameters for the quantitative analysis are optimized. The biological compounds under investigation can be determined with the aid of cathodic adsorption stripping voltammetry in presence of Cu(II) at concentration of the order of magnitude 10^{-10} M.

VOLTAMMETRIC STUDY AND DETERMINATION OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTIONS

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Hydrogen peroxide is getting increasingly popular as an oxidising/bleaching reagent for several industrial uses (bleaching textile and paper pulp, disinfectant for swimming pools...) This popularity is due to the ecological advantages that hydrogen peroxide has in comparison with its competitors. Unlike the chlorine based reagents, peroxide has no reaction products that are harmful for the environment.

The increasing industrial use of hydrogen peroxide leads to a growing demand for techniques, able to monitor the peroxide concentrations. In the ideal case this would be a continuous measuring method. Earlier investigations carried out in our department already lead to the development of a sensor for hydrogen peroxide specifically suited for use in alkaline textile bleaching solutions, by P. Westbroek. A sensor with a much wider application area would be desirable. The development of such an amperometric sensor is the purpose of the work reported here. The electrochemical techniques used in this study, are linear sweep voltammetry, cyclic voltammetry and chronoamperometry. Different electrode materials were investigated and platinum appears to be the most promising. Special attention is being given to the influence of pH on the voltammetric behaviour of hydrogen peroxide. Kinetic data derived from the experimental results are used to obtain information about the mechanism of the electrochemical reduction and oxidation of hydrogen peroxide

CARBON PASTE ELECTRODES MODIFIED WITH INORGANIC MERCURY COMPOUNDS AND THEIR USE IN POTENTIOMETRIC STRIPPING ANALYSIS OF HEAVY METALS

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One of the many different fields of using the carbon paste electrodes (CPEs) is their exploitation, among the other types of carbon substrates, as a support for mercury film electrodes (MFEs) [1]. The mercury electrodes can be replaced by MFEs achieving nearly the same, sometimes better, analytical performance, depending on the analytical task. We focused on the ability of bulk modifying of the carbon paste by inorganic mercury compounds, exploiting the characteristic properties of CPEs. The mercury film is then generated from the surface of electrode by applying the sufficient negative potential during the accumulation step of stripping analysis, thus in fact the MFE is formed [2, 3]. Once the content of carbon paste is modified such a way, the CPE can be used repeatedly till the paste becomes depleted.

Several inorganic mercury compounds and pasting liquids were used to test the modified CPEs using constant current potentiometric stripping analysis of cadmium, lead and zinc. Also, the effect of supporting electrolyte was studied. Results obtained were evaluated and optimal compositions of CPEs and conditions for analysis were used to calculate detection limits, standard deviations and recoveries for heavy metals. Comparison of results obtained with CPE preplated with mercury in pure mercury(II) solution was made. The CPEs modified with mercury compounds exhibited good electroanalytical properties and allow minimizing the need of handling the mercury electrodes or the mercury containing solutions during analysis.

References

1. Švancara I, Pravda M, Hvizdalová M, Vytras K, Kalcher K (1994) *Electroanalysis* 6:663
2. Guo SX, Khoo SB (1997) *Environ Monit Assess* 44:471
3. Metelka R, Vytras K, Bobrowski A, J *Solid State Electrochem*, submitted for publication

APPLICATION OF ELIMINATION VOLTAMMETRY TO THE ELECTROANALYSIS OF AN ADSORBED SUBSTANCE

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Elimination voltammetry with a linear scan rate (EVLS) provides elimination of one or two selected currents from the linear scan voltammetry (LSV) results. The elimination relies on an elimination function formed by a linear combination of total currents that are measured at different scan rates [1,2]. The necessary condition to the elimination is the expression of the eliminated current in the form of a product with two functions: the scan rate function independent of electrode potential and the electrode potential function independent of scan rate. Elimination functions contain the charging current, I_c , the reversible current for substances transported only by linear diffusion, I_r , and the pure kinetic current, I_k .

In comparison with ordinary voltammetry the EVLS provides some substantial advances: (a) the expansion of available electrode potential range, (b) the increase of current sensitivity and (c) the improvement of the peak resolution. (b) and (c) result from the fact that the elimination of kinetic and charging current decreases the irreversible current width and increases the peak height. This effect is particularly pronounced in the case of adsorbed substance.

The theoretical curves of an irreversible current of the adsorbed substance were calculated for three elimination functions. A greater difference between diffusion and adsorption was exhibited by the function that eliminates I_k and I_c and conserves I_r . The above procedure was applied to oligonucleotides and nucleic acids. While a slight hints of a peak can be seen on CV curves, this elimination gives sharp peak-counterpeak signals belonging to the strong depolarizator adsorption, according to the theory. This elimination function for adsorbed substances can be useful for analytical applications, particularly for adsorptive stripping voltammetry with electrochemical irreversible systems.

References

- [1] O. Dracka, J. Electroanal. Chem., 402 (1996) 18.
- [2] L. Trnková and O. Dracka, J. Electroanal. Chem., 413 (1996) 123.

This work was supported by grant 204/97/K084 from the Grant Agency of the Czech Republic.

SENSOR FOR ON LINE MEASUREMENT OF CHEMICAL OXYGEN DEMAND BASED ON ROTATING RING-DISC MULTIPULSE VOLTAMMETRY

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An indication for the organic load of industrial waste water can be obtained by determination of the BOD and COD values. Unfortunately the present methods for COD determination are off line, consume ecologically unfriendly substances ($\text{Cr}_2\text{O}_7^{2-}$, H_2SO_4) and have a poor precision and accuracy. This research shows a possibility to obtain the COD of waste water in a relatively short time making use of aggressive radicals produced in situ at the disc of a ring-disc electrode configuration.

At the surface of a rotating Pt-ring Pt/PbO₂-disc electrode a square wave potential step ($\square\square\square$) is applied (step from 1.4 to 1.85 V vs. SSE). At the ring electrode a constant potential is applied, situated in the limiting current plateau of the oxygen reduction. At the potential of $E_{D,1}=1.4\text{V}$ no oxygen is produced at the disc electrode and the obtained ring current I_R' corresponds to the reduction of dissolved oxygen. At $E_{D,2}=1.85\text{V}$ the oxygen evolution reaction occurs and results into a disc current I_D and a ring current I_R . The latter corresponds to the reduction of dissolved oxygen and a fraction (determined by the collection efficiency N_0) of oxygen that is produced at the disc electrode. After calibration of the rotating ring-disc electrode with CH_3COONa standard solutions the COD of solutions with unknown composition can be obtained by

$$\text{COD} = k \left[I_D - \left(\frac{I_R - I_R'}{N_0} \right) \right]$$

where k is a constant determined by calibration.

Experimental results showed that it is possible to measure the COD on line with a precision better than 2% and within a range of 50 up to 14 000 mg L^{-1} , representative for actual COD values of industrial waste water. Recently promising results have been obtained for waste water samples from a distillation plant (COD range : 1000 – 5000 mg L^{-1}) and a photo developing site (COD range : 7000 – 20 000 mg L^{-1}).

POLAROGRAPHIC AND VOLTAMMETRIC DETERMINATION OF SELECTED AZO DYES

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Azodyes, which form the largest group of organic dyes, constitute more than 35% of the global production of all dyes and thus are encountered in our living, working and natural environment. Unhydrolysed reactive azo dyes have long half-lives in near neutral solutions and as they can react with proteins they can pose an environmental threat. Therefore, there is an ever increasing demand for determining the trace amounts of both reactive and hydrolysed dyes in environmental samples. Because of the easy reducibility of azo group, modern polarographic and voltammetric methods are suitable for the determination of trace amounts of these substances in the general environment in the vicinity of production plants [1]. Within the framework of the systematic study of polarographic and voltammetric behaviour of reactive azodyes, we devoted attention to the determination of trace amounts of some reactive azodyes, namely Reactive Orange 4, Reactive Orange 13 and Direct Blue 71 and we have found optimum conditions for the determination of these substances using Tast polarography in the concentration range $2 \cdot 10^{-6}$ - $1 \cdot 10^{-4}$ mol.l⁻¹, differential pulse polarography in the range $2 \cdot 10^{-7}$ - $1 \cdot 10^{-4}$ mol.l⁻¹, differential pulse voltammetry on hanging mercury drop electrode in the range $2 \cdot 10^{-7}$ - $1 \cdot 10^{-4}$ mol.l⁻¹ and adsorptive stripping voltammetry in the range $2 \cdot 10^{-8}$ - $1 \cdot 10^{-7}$ mol.l⁻¹.

REFERENCES

[1] Zima J., Barek J., Moreira J.C., Mejstřík V., Fogg A.G.: Crit.Rev.Anal.Chem. **1999**, 29(2), 125 -129.

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POTENTIOMETRIC STRIPPING ANALYSIS OF COPPER USING GOLD ELECTRODES FROM RECORDABLE COMPACT DISCS

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A new, versatile and easy way to obtain gold electrodes (CDtrodes) from recordable compact discs (CDs) and their applications for trace copper quantification in drinking water and sugar cane spirits are presented. The new electrodes shown performance comparable to commercial gold electrodes, with superior versatility and very low cost. Recordable CDs are constituted by a polycarbonate base on which a thin recording photosensitive dye is deposited. On this layer, a mirror-like film of gold is fixed. The thickness of this film is between 50 and 100 nm and his superficial area is about 100 cm². This gold layer is covered again, usually by two polymeric layers. To expose the gold surface, the two protective films are chemically removed with concentrated nitric acid. Each recordable CD can originate many gold electrodes by cutting the disc in slices with a paper guillotine or a large scissors. After the removal of the protective film, the electrode work area can be defined using a layer of epoxy, PVC resin or nitrocellulose enamel. A characterization study involving the purity of these gold films and the electrochemical response of the CDtrodes was presented previously [1]. CDtrodes were used successfully for quantification of mercury by flow injection analysis [2].

The quantification of copper in drinking water and sugar cane spirits was made in a stationary cell, using chloridic acid solution (0.05 mol L⁻¹) as supporting electrolyte. Preliminary studies involving synthetic samples demonstrate a the detection limit (10 min deposition) of 0.03 µg/L. The reproducibility of 20 repetitive stripping potentiograms, for 25 µg/L copper solution (60 s deposition) shown a standard deviation of 1.8 %. The amount of copper found in drinking water collected in the lab (at different days) was situated between 4 and 7 µg/L. The copper content in samples of five different sugar cane spirits were evaluated and the results were similar with the ones obtained by atomic absorption spectrometry.

References

1. Richter E M, Kume G H, Mioshi R N, Augelli M A, Angnes L (1999), XI Simpósio Brasileiro de Eletroquímica e Eletroanalítica – Santa Maria, Rio Grande do Sul, Brasil – Resumos, p.72
2. Richter E M, Kume G H, Mioshi R N, Augelli M A, Angnes L., Fresenius J. Anal. Chem. accepted for publication

A.C. STRIPPING VOLTAMMETRY HETEROCYCLES AT TRACE LEVELS WITH ADSORPTION ON MERCURY HANGING DROP ELECTRODE

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The benzodiazepine, pyrazine, pirimidine and mercaptopurine drugs are of great clinical interest. It is possible to decrease the detection limit of nitrogen, sulfur and oxygen heterocycles using their adsorptive accumulation on mercury hanging electrode surface. In order to decrease the detection limits of heterocyclic compounds the conditions of their accumulation on mercury drop electrode have been investigated.

The highest affinity to mercury surface corresponds to zero charged potential, uncharged forms are adsorbed. Adsorption is described by generalized Frumkin' isotherm. Adsorption energy is equal to 40–50 kJ/mol, attraction coefficients change in the range of 0.13–1.93. Adsorption parameters fully determine the analysis metrology. The slopes of the calibration curves are correlated by adsorptivity: if β is equal to 10^7 – 10^8 l/mol, the detection limit can be about 10^{-10} – 10^{-11} mol/l.

The length of linear part of the calibration curves is connected with the attraction factor (monolayer adsorption parameter, a). Oxazepam ($a=0.69$) and chlorodiazepam ($a=1.9$) can be determined in concentration range $5 \cdot 10^{-10}$ – $2 \cdot 10^{-6}$ and $4 \cdot 10^{-9}$ – $5 \cdot 10^{-7}$ mol/l, respectively. Compounds with low attraction constant (triamteren, folic acid) have linear calibration curves for the concentration range of the order of 3.5. Attraction constant of riboflavin and azaphene is over one. Concave initial part of isotherm decreases the concentration range of these substances up two order.

Using mercaptopurine affinity of mercury for nitrogen and sulphur has been studied: introduction of a sulphur atom into purine structure makes adsorption irreversible. By its adsorption behaviour mercaptopurine is closer to thiocarbamic acids than to nitrogen containing heterocyclic compounds. High adsorption energy of pirimidine derivatives allows to reach detection limit of 10^{-12} – 10^{-11} mol/l by four minutes accumulation on electrode.

A.c. stripping voltammetry in combination with adsorption preconcentration provides as low detection limits for antraquinone and tetracycline derivatives as $(2-4) \cdot 10^{-10}$ mol/l. In accordance with this method the detection limit is three order of magnitude under that of differential pulse polarography with dropping mercury electrode.

APPLICATION OF ANODIC STRIPPING VOLTAMMETRY TO THE INVESTIGATION OF THE HEAVY METAL COMPLEXATION IN THE DNIEPER WATERBODIES

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Dissolved forms of zinc, lead and cadmium in water of the Dnieper reservoirs and the Dnieper-Bug estuary are mainly present in the form of complexes with dissolved organic matter (DOM). Depending on the season, the degree of heavy metal (HM) complexation varies, reaching a maximum of 66 – 98 % of the total content of their dissolved forms. As our investigation showed, complexation in the Dnieper waterbodies is a highly intensive process with participation of naturally occurring DOM, both of allochthonous and autochthonous origin.

Complexation plays the dominant role in detoxification of HM compounds in the Dnieper reservoirs. For the purpose of evaluating the potential detoxification influences of DOM its complexing ability (CA) was studied. CA allows an evaluation of the maximum possible total concentration of organic ligands in natural water and, more precisely, of their free coordination centers which can bind HM ions into complexes. The quantitative expression of CA is a concentration (in $\mu\text{mol/liter}$ or $\mu\text{g/liter}$) of the part of metal, which pass to the bound state in condition of "saturation" of DOM active complexing centers by metal ions. Measurement of CA presupposes the establishment of equilibrium in the system, and equilibrium can be reliably identified only when the complexation kinetics of the metal in natural water is known.

The concentration of uncomplexed metal (free ions) was determined by highly sensitive anodic stripping voltammetry. This method together with the gel-penetration and ion exchange chromatography was used to the investigation of Zn, Pb and Cd distribution among the complex compounds with DOM of different molecular weight and chemical nature.

Complexing ability undergoes a seasonal change that is conditioned by the different component composition of DOM in the Dnieper reservoirs. In springtime CA is lowest and this can cause worsening of the water quality owing to increasing concentrations of free metal ions, the most toxic form of heavy metals. In original water, the major part of investigated metals (60 – 80 %) is in the fraction of humic substances. In condition of "saturation" of active coordination centers by HM ions, the complexation proceeds mainly at the expense of relatively low molecular weight ligands (< 5,000 daltons).

INDIRECT VOLTAMMETRIC MONITORING OF THE EFFICIENCY OF THE PHOTODEGRADATION OF EDTA MEDIATED BY TiO_2 IN SUSPENSION

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A well known advantage of electroanalysis on spectrophotometry and other techniques is that measurements are usually not disturbed by the turbidity of samples such as suspensions and emulsions. By studying the effect of the presence of TiO_2 suspensions in polarography, we have observed that well defined polarograms are obtained for heavy metal ions or organic electroactive species. Nowadays, TiO_2 is broadly employed in research on the treatment of industrial wastewater, looking for the acceleration of the photodegradative abatement of organic load by solar radiation. TiO_2 (*anatase*) is an efficient photocatalyst and it has been immobilized onto various types of support, although with some difficulties and shortcomings. Consequently, in the majority of cases, it is used as a suspension or gravity sedimented on large area surfaces. The interference of colloidal particles during the analytical monitoring of the efficiency of these treatments, thus, cannot be disregarded, making voltammetric techniques more attractive than spectroscopic or chromatographic ones. To follow TiO_2 mediated photomineralization processes by voltammetry, EDTA was used as a model organic pollutant, and its sequestering power of Cd(II) ions was measured during treatment. A photochemical was assembled and consisted of: i) a medium pressure mercury lamp (400 W nominal power output, 10 cm length), ii) a PTFE tube coiled around the lamp and used as irradiation chamber (8 ml volume); iii) a thermostating system and iv) an optional O_2 -enrichment device. 20-ml aliquots were treated irradiated and the degradation of aqueous EDTA solutions (1 mmol dm^{-3} in 10 mmol dm^{-3} NaAc/HAc buffer) was observed by the recovery of the pulse polarographic wave of the released Cd(II) ($100 \text{ } \mu\text{mol dm}^{-3}$), at $-0.7 \text{ V vs. Ag/AgCl}$. Similar, but less precise results, were obtained by recording the Hg oxidation wave caused by the EDTA. The effect of a number of factors is being investigated: TiO_2 content, O_2 concentration, pH, temperature and light intensity, presence of electron/radical/hole scavengers and metal adsorption/reduction onto the TiO_2 particles. Current results indicate that the voltammetric procedure should serve for nearly real time monitoring of large scale TiO_2 mediated photoreactors and that the lab prototype has a great potentiality also a for strictly analytical application: fast mineralization of organic matter in water samples, in substitution to conventional UV irradiation or microwave oven digestion.

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CATHODIC STRIPPING VOLTAMMETRY DETERMINATION OF DIMETHILSULFIDE IN CONDITION OF COMPLEX WITH MERCURY (II) CHLORIDE

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The mode of determination of toxic organic sulfide - dimethylsulfide was devised. Dimethylsulfide is present, for the most part in drain of pulp and paper and oil-refining industry. The limiting value of dimethylsulfide in bodies of water is 0.01 mg/L or 1.6×10^{-7} M and 0.03 mg/L in drain after the composite cleaning. The modes of determination of dimethylsulfide on this level of concentration is known in the literature. This is method of spectrophotometry, which required pre-loaded concentrating by extraction [1] and method of gas chromatography with a flame-fotometric detector [2]. The determination of dimethylsulfide by method of cathodic stripping voltammetry have a range of concentration from 9×10^{-6} to 5×10^{-4} M in basic solutions on the mercury electrode with silvers foundation [3]. Complex of dimethylsulfide with mercury (II) is known in the literature. Mercury (II) chloride is added for increases on 3-4 orders the sensitivity of determination and reduces preventive influence of many inorganic ions in the solution. $Sr=0.20$ for the concentration 9×10^{-10} M ($t_d = 60$ c), what indicated on possibility of determination of more low concentration of dimethylsulfide.

References

1. Zatuchnaja L.A., Kremer V.A., Tsvindina G.F.//Jurn. anal. chem. 1977.v.32. ; 7 P.1431.
2. Andreac M.O., Barnard W.R.//Anal. Chem. 1983. v.55. ; 4. P.608_612.
3. Leites E.A., Katjuhin V.E., Anismova L.S.//Izvestia AGU. 1998. ; 1.

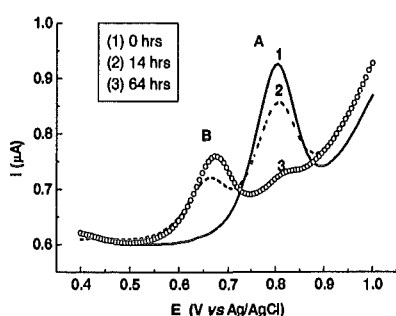
VOLTAMMETRIC ANALYSIS OF 1,4-DIHYDROPYRIDINES: APPLICATION TO DEGRADATION STUDIES

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The stability of a pharmaceutical compound is of crucial importance due to its relevance in the therapeutic efficacy and the possible toxicity generated by degradation products. Often it is not sufficient to determine the concentration of the active principle, but also to determine if degradation have occurred and the nature of the degradation products.

In this work a differential pulse voltammetric method was developed to follow the kinetic of hydrolytic degradation of two pharmaceutical compounds belonging to the 1,4 dihydropyridine family: nitrendipine and nisoldipine.



These molecules have two electroactive centres; the nitroaromatic group, which can be reduced and the 1,4 dihydropyridine ring, possible to be oxidised with aromatization of the ring. To follow the time course of degradation only the oxidation on a glassy carbon electrode proved to be useful. In figure 1 we can observe the decrease of the nitrendipine peak (A) and the appearance of the degradation products. (B)

Figure 1. Evolution of the differential pulse voltammetric peaks for the degradation of nitrendipine at pH 12 and 80°C. A: nitrendipine (0.807 V); B: hydrolysis products (0.662 V). Supporting electrolyte: phosphate buffer 0.25 M-ethanol 20%, pH 6.8, glassy carbon working electrode with electrochemical pre-treatment.

The following analytical parameters were established: linear dependence between current and concentration for levels between 5.0×10^{-6} and 6.0×10^{-5} M, Limit of quantitation (M) = 4.0×10^{-6} , Limit of detection (M) = 1.5×10^{-6} , Recovery (%) = 98.5, RSD (%) = 1.5

The degradation kinetic was of pseudo-first order and decay constants were determined at different pH's and vehicles. Arrhenius activation energies also were calculated.

It can be concluded that the voltammetric measurements can be applied to degradation studies.

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Poster Contributions

Session E

SENSITIVITY AND SELECTIVITY IN NON-AQUEOUS CAPILLARY ELECTROPHORESIS WITH ELECTROCHEMICAL DETECTION

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Capillary electrophoresis in combination with electrochemical detection (CE-ED) is often employed when high separation efficiency and low detection limits are demanded [1]. However, there are two major problems associated with CE-ED: the interference of the high voltage separation field with the detection circuit and the maintenance of a clean, reproducible surface of the detection electrode. Non-aqueous CE (NACE), in which aqueous buffers such as phosphate or borate are replaced by electrolyte systems based on organic solvents, has in this context several advantages over "aqueous" CE [2]. NACE is well suited to circumvent the need for decoupler devices by minimizing interferences using low conductivity non-aqueous electrolytes. Organic solvents like acetonitrile (AN) also reduce the risk of electrode fouling [3]. Additionally, the accessible potential window in AN is larger than in water. Therefore, higher detection potentials can be applied which extends the scope of ED to analytes that are difficult to oxidize (reduce) and leads to an increase in sensitivity. These characteristics of NACE-ED were applied to the analysis of various drugs of abuse including amphetamines and cannabinoids. For MDA and MDMA, two amphetamines frequently found on the illegal drug market, detection limits of 3.6 ng/ml and 2.7 ng/ml were found, which is between 2 and 3 orders of magnitude lower compared to UV-detection. An improved separation selectivity of NACE compared to "aqueous" CE results from shifts in equilibrium constants [2]. Since the choice of the separation buffer also effects the detection characteristics several non-aqueous buffer compositions for the analysis of amphetamines and cannabinoids were investigated and compared.

References

1. B.B. Anderson, A.G. Ewing, J. Pharm. Biomed. Anal. 19 (1999) 15.
2. S.H. Hansen, J. Tjørnelund, I. Bjørnsdottir, Trends Anal. Chem. 15 (1996) 175.
3. F.-M. Matysik, Electrochimica Acta, 43 (1998) 3475.

CHARACTERIZATION AND PRACTICAL TEST OF A NEW DUAL THIN-LAYER CELL USED FOR COMBINATION OF DEMS AND EQCM

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We developed a new dual thin-layer cell, which can be used under flow conditions for simultaneous measurements of the mass change at a quartz crystal used as the electrode and the mass spectrometric detection of volatile reaction products [1]. This is demonstrated for the oxidation of preadsorbed CO at a polycrystalline platinum and PtRu-alloy electrode. The results show, that in case of the PtRu-alloy electrode even at potentials near the hydrogen evolution anions are still adsorbed.

To test the applicability of this cell for various substances, solutions of species (with different partial pressures in aqueous solution) were led through the cell and the mass spectrometric current was recorded as a function of the flow rate u . As expected, sensitivity is highest for gases and lowest for hydrophilic substances. Variation of the flow rate during the bulk-oxidation of CO at polycrystalline platinum leads to a collection efficiency N (ratio of electrochemical produced species to mass spectrometric detected species) of 50 % even at such high flow rates, where the time constant is lower than 2 seconds. Thus, the sensitivity is sufficient for the mass spectrometric detection of species being stripped from preadsorbed monolayers of organic compounds. This is clearly demonstrated by the fact that even desorption products of naphthalene, desorbing from polycrystalline platinum as naphthalene and as partially hydrogenated tetraline, can be detected. Tetraline and the fully hydrogenated decaline can be seen at polycrystalline platinum as hydrogenation products from bulk solution at constant negative potentials, whereas in the case of Pt(111) no hydrogenation occurs.

References

1. H. Baltruschat, *Differential Electrochemical Mass Spectrometry as a Tool for Interfacial Studies*; p.577-597; *Interfacial Electrochemistry*; edited by. A. Wieckowsky; Marcel Dekker Inc., New York 1999

THE OENOLOGIC MONITOR CELL

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In spite of utmost care observed during vinification it happens every now and then that enhanced levels of metal concentrations occur in the final product. Even the faintest traces of certain metals may deteriorate the delicate balance of ingredients. This results in an organoleptic unsatisfying taste long before the critical concentration for optically visible dullness caused by metals is reached. The physico-chemical environment of the wine determines the oxidation state and binding forms of the metals in the liquid. To characterize the wine in that respect we here propose the use of the "oenologic monitor cell". Different electrodes are combined with various electrochemical measuring techniques.

It is possible to distinct different wines in a rapid, and simple way at minor expenses. By measuring the following parameters: redox potential, pH, cyclovoltammograms at different voltammetric working electrodes, the wines are classified according to their respective level of quality and the year of harvest. By the aid of ion sensitive electrodes we approximate the fraction of "free ions". Furthermore one gains information about metal concentration, binding state and electrochemical reactive organic compounds as well by usage of voltammetric measurements (direct, invers) with different working electrodes and techniques (DPP, AC₁). The key advantage of the "oenologic monitor cell" is that the measurement takes place directly in the matrix wine without any substantial changes of it. This is due to the very minute takeover of material at the electrodes. Besides this data which allow a direct characterisation (of the wine status) the cell opens up the possibility to study the interdependencies of the measured parameters in situ with almost no time lag. This is performed by forced variation of one parameter while the corresponding change of all others is monitored.

This improves the understanding of the dynamic system "wine". It is expected that the elucidation of the processes which lead to mistaste caused by metals will result in concrete advice for the practitioner how to avoid those effects. The stability of the wine will be enhanced without laborious treatment which in turn means a substantial step forward for wine quality. Construction and accessory equipment of a "oenologic monitor cell" and first results as well are presented.

ELECTROCHEMICAL PRETREATMENT OF WATER SAMPLES IN A FLOW-THROUGH DISCRETE STRIPPING VOLTAMMETRIC SYSTEM

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An actual concentration of an element in a sample cannot be determined without eliminating the interfering effect of the matrix through its destruction. For this purpose a method was developed [1] for electrochemical sample pretreatment in stationary laboratory conditions using a two-chamber cell. This method can be realized in an automatic regime in a single-chamber four-electrode flow-through discrete cell, which is outfitted with a long-lived working electrode having a renewable surface. A standard three-electrode scheme of voltammetric measurements was supplemented with a fourth electrode, which represents the working sample pretreatment electrode. As a result, sample pretreatment and measurements can be made in sequence in a single cell. Oxidation current and the working electrode potential are preset independently during sample pretreatment. If a modified electrode is used, its surface can be formed during sample pretreatment. An IVA-7 stripping voltammetric analyzer controls the whole process. This analyzer ensures computer-aided assignment of measurement and sample pretreatment parameters, processing of analytical signals (responses), automatic detection of peaks, and concentration calculation. This device is indispensable for automatic laboratory and commercial (including remotely controlled) monitoring systems.

A model solution containing (mg/l) Triton (0.25), polyethylene glycol (0.25), phenol (0.05), diethylene amine (0.5), glucose (2.5), urea (0.15), humic acid (2.5), fulvic acid (30), butyric acid (250), trypsin (15), Cd(II) (0.002), Pb(II) (0.004), Cu(II) (0.01), and Zn(II) (0.02) was analyzed after electrochemical pretreatment. The recovery (%) was 100 (Pb), 103 (Cd), 110 (Cu), and 98 (Zn). Electrochemical pretreatment was performed at oxidation current of 2.5 mA for 5 minutes.

Reference

1. Brainina Kh.Z., Khanina R.M., Roitman L.I. *Analyt. Letters*, 1985, **18**, 117 – 134

LONG PATH SPECTROELECTROCHEMICAL FLOW CELL WITH INEXPENSIVE GOLD ELECTRODES

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Since the advent of spectroelectrochemistry in the UV-visible region [1] a multitude of cells have been proposed and evaluated in the literature. Most cells are intended for stationary operation, but flow cells are also needed, for example, for analytical purposes, and the available designs are difficult to construct or to adapt to conventional spectrophotometers [2,3].

The new cell described here fits directly into conventional glass, plastic or quartz cuvettes with 1 cm optical path. Gold working and auxiliary twin electrodes were obtained by simply cutting 2 pieces of 1.0 x 5 cm from recordable CDs (BASF or Toshiba, gold colored). The polymer film was stripped from the gold layer with nitric acid [4]. These electrodes are very inexpensive (actually, disposable), flat and clean, requiring no polishing. They were glued onto acrylic pieces of the same size (total thickness, 3.5 mm) and mounted face to face in the cuvette. A scratch, in form of an L, on the gold layer of each electrode, delimitates the lowest 1.0 x 1.0 cm area as working electrode and the remaining surface, as auxiliary electrode. The flow enters the cell through a capillary PTFE tube embedded in a groove at the back side of one electrode, lending to the bottom of the cell, and is sipped out at the top. The capillary tip of a miniaturized reference electrode (Ag/AgCl) is inserted into the cell. At a flow rate of 1 ml min⁻¹, aprox. 30% of injected *o*-tolidine was oxidized, as measured at $\lambda = 438$ nm. The cell was found very suitable for flow injection analysis (FIA). The effects of parameters like applied potential, analyte concentration, flow rate and injected volume were evaluated. The relative standard deviation ($n = 15$) for FIA absorbance peaks was 0,46%.

In conclusion, the new spectroelectrochemical cell gathers very attractive features: its construction is straightforward and inexpensive; gold electrodes (cutted from CDs) are fitted directly into conventional cuvettes, used in any spectrophotometer; measurements are stable and reproducible under flow operation; the upward stream restricts O₂ access, of value when degassed samples are studied; the cell presents high potentiality for future FIA applications.

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References

1. Kuwana, T.; Darlington, R. K. and Leedy, D. W.; *Anal. Chem.*; **1964**, 36, 2023.
2. Yupeng Gui, Steven A. Soper, and Theodore Kuwana; *Anal. Chem.*; **1988**, 60, 1645.
3. Chen, H.-Y. and Long, Y.-T.; *Anal. Chimica Acta*; **1999**, 382, 171.
4. Richter, E.M.; Kume, G.H.; Mioshi, R.N.; Angnes, L.; Augelli, M.A.; *Fresenius Z. Anal Chem.* **2000** (*in press*).

CONTACTLESS CONDUCTOMETRIC AND SIMPLIFIED AMPEROMETRIC AND POTENTIOMETRIC DETECTION FOR A PORTABLE CAPILLARY ELECTROPHORESIS INSTRUMENT

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For robustness the amperometric and potentiometric detection modes are carried out in a fixed wall-jet cell without decoupler. Both methods exploit the electrophoretic ground electrode as combined reference and counter electrode, which is very stable because of the water hydrolysis enforced by the electrophoretic current and this greatly simplifies the detection cell. The approach should make the highly promising amperometric detection more widely accessible. Potentiometric detection was carried out with miniature coated-wire and copper electrodes.

The new contactless mode of conductivity detection is also inherently very sturdy. The arrangement furthermore enables its combination with either the amperometric or potentiometric mode for concurrent measurements.

The three electrochemical detection methods can be considered complementary. Conductivity detection is universal but works best for small inorganic ions with high mobility while potentiometric detection is suitable for larger lipophilic and organic ions. Amperometric detection allows excellent detection limits but is only possible with electroactive ions. The availability of the three methods in the same instrument allows for great versatility. A small portable capillary electrophoresis instrument, which includes a 30 kV-high voltage supply and the detection electronics has been designed and built. The device is suitable for field-measurements as it contains rechargeable batteries as an independent power source. A variety of applications to inorganic as well as organic analytes will be presented.

ELECTROCHEMICAL PROCEDURE FOR DETERMINATION OF MERCURY IN WASTE SOIL SAMPLES

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The electrochemical procedure for the determination of mercury in waste soil samples consists of two parts. The main aim of the first one is to move the mercury from soil to a solution. The second part of the procedure is an electrochemical determination of mercury on gold electrode.

In the first part of the procedure, mercury is thermally released from its compounds in a temperature of about 900°C. During this operation, a sample is placed on a quartz boat inside quartz probe. Then the mercury vapors are condensed on the probe walls in low temperature. Subsequently, the mercury is dissolved in an acidic mixture. The solution, after diluting, is irradiated with UV radiation that oxidizes the organic matter which is realized from the soil simultaneously with the mercury. After these operations, the solution is ready for the electrochemical determination.

The electrochemical determination consists of three steps: electrode activation, mercury reduction on electrode surface and measurement with DPSV. The first two steps of electrochemical determination are simpler when the flow system is applied. System consists of a peristaltic pump, a two-way valve, and a wall-jet electrochemical cell.

Mercury is an element that may cause many analytical problems, such as possibilities of its loss or contamination. In the determination of mercury in the environmental soil samples, contamination is a very important problem. The most advantageous in the suggested method are: a good prevention from mercury contamination (because of a very simple and effective thermal cleaning of the equipment), a low cost of analysis, a low cost of apparatus, a relatively short time of sample preparing, the possibility of using cheap electrochemical detection of mercury in the last step of determination.

RAPID AND SENSITIVE DETERMINATION OF 4-NITROPHENOL, 3-METHYL-4-NITROPHENOL, DNOC, PARATHION-METHYL, FENITROTHION AND PARATHION-ETHYL BY LIQUID CHROMATOGRAPHY WITH ELECTROCHEMICAL DETECTION

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Liquid Chromatography with electrochemical detection has been used to determine various nitropesticides: DNOC, fenitrothion, parathion (methyl and ethyl) and some of their main metabolites such as 4-nitrophenol for parathion (methyl and ethyl) and, 3-methyl-4-nitrophenol for fenitrothion by using dual porous graphite electrode (reductive- oxidative) with coulometric detection. The analysis of them in river water samples has been performed without a preconcentration step.

This technique overcomes the problems of high background currents and oxygen interference, observed in the direct reductive detection of organonitro compounds. A Nova-Pak C18 column (150x3.9 mm, 4 μ m) and a Coulochem II (ESA) model 5200 detector (electroanalytical cell ESA model 5011 with conditioning cell model 5021) were used. According to the hydrodynamic curves of the pesticides in the reductive and oxidative mode in the porous graphite electrode, we have selected the following conditions: E (conditioning cell) = -600 mV, E1 = -1300 mV and E2 = +700 mV. A cleaning step of the electrode 1 is made prior to injection of the samples standard, applying a potential of +1300 mV during 7 min.. The influence of mobile phase composition and flow rate has been studied. The mobile phase used as optimum is 60:40 Methanol: 0.01 M aqueous solution of sodium perchlorate with 0.5% glacial acetic acid at a 1ml/min flow rate. The oxygen of the mobile phase was removed with a vacuum system on-line. The detection limits of these compounds ranged between 0.05 and 0.14 ppb. The analysis of the pesticides in river water samples has been performed without a preconcentration step. The recovery values were between 96 and 112 % at the fortification level of 0.5 ppb in river water and their relative standard deviations were between 1 and 15 %.

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PREPARATION OF IR-DOPED TITANIUM ANODES AND THEIR INVESTIGATION BY THE DROPLET CELL

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DSA (Dimension Stable Anodes) are widely used as anodes for oxygen evolution because of their life-times of some years. On a very rough Ti substrate the catalyst layer of e.g. an IrO₂-doped corrosion resistive matrix of Ti- and Ta-oxides is deposited. This active layer is produced by repeated thermal treatment of hydrochloric or organometallic precursors of Ti, Ta, and Ir at high temperatures. By means of the droplet cell layers from different production steps were analyzed by current-potential- and charge-potential-curves or impedance spectroscopy. From oxygen evolution, hydrogen evolution, and the redox process of the Ir oxide the structure and the electronic or ionic conductivity were evaluated. The droplet cell was also very useful in investigating the processes of ageing of the anodes.

References:

- R. Otagawa, M. Morimitsu, M. Matsunaga, *Electrochim. Acta* 44 (1998) 1509
- G. Foti, C. Mousty, V. Reid, C. Comninellis, *Electrochim. Acta* 44 (1998) 813
- M. M. Lohrengel, *Electrochim. Acta* 42 (1997) 3265
- M. M. Lohrengel, A. Moehring, M. Pilaski, *Fresenius J. Anal. Chem.*, submitted

ELECTROCHEMICAL PRETREATMENT OF GOLD TO OBTAIN A REPRODUCIBLE SURFACE FOR MOLECULAR SELF-ASSEMBLY

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Gold is a suitable substrate for the formation of self-assembled monolayers (SAMs) from thiols, sulfides, and disulfides. These SAMs can be used as intermediate layers for the coupling of a wide range of molecules, including enzymes and antibodies. The state of the surface, including the surface roughness, is very important for the reproducible formation of high-quality self-assembled monolayers on gold. As a consequence, this may be an important factor in the reliable production of affinity biosensors based on SAMs.

The described pulsed-potential pretreatment procedure can, in a reproducible way, reduce the surface roughness of mechanically polished polycrystalline gold electrodes with a factor 2 to 3. The developed procedure, in which the gold is alternately oxidized and reduced, has been optimized for use in a flow system (100 mM phosphate buffer pH 7.4). The influence of the pretreatment procedure on the surface roughness of the electrodes has been studied by in-situ oxygen adsorption measurements using cyclic voltammetry. The most effective pulse regime in producing a gold surface with a reproducible and relatively low surface roughness, is a triple-potential pulse waveform, with potentials of +1.6, 0.0, and -0.8 V vs. SCE, and pulse widths of 100 ms for each potential. Prolonged pulsing for 2000 - 5000 s with the gold working electrode in a flow-through cell showed an electropolishing effect, i.e. a decrease of the roughness in time. Flow conditions are very important: the roughness decreased faster at higher flow rates, while an increase was observed without flow. A process of reconstruction and dissolution of gold during application of the potential pulses under flow conditions is assumed to account for the observed phenomena.

ELECTROCHEMICAL DETECTION IN CAPILLARY ELECTROPHORESIS FOR THE ANALYSIS OF WINE

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Fast, reliable and cost efficient analytical methods are needed for controlling the production of wine. Capillary electrophoresis (CE), which has been established as an alternative method to liquid and gas chromatography in many fields of application, may also be used for this application. High performance electrochemical detection at microelectrodes in capillary systems allows to investigate even small volume samples in the nanolitre range with high reproducibility and a large sample throughput at moderate costs for the analytical equipment [1]. Only recently, a simplified electrode arrangement and an electronic layout were introduced [2] which resulted in a low cost transportable CE device [3].

In this investigation we have been concentrating on relevant components of wine characterising fermentation and ripening processes (sugars and organic acids) as well as storage conditions (sulphite). Preliminary experiments have shown, that in contrast to platinum and gold electrode materials only copper microelectrodes are suited to analyse all of the components of interest. These microelectrodes (prepared by sealing 50 μm $\varnothing$ Cu wires in silica capillaries) were positioned at the outlet of the separation silica capillary in a miniaturised amperometric measuring cell which also contained a Pt counter electrode carrying the electrophoretic current [2]. The addition of cetyltrimethylammoniumbromide (CTAB) to the buffer system proved to be important for modifying the electroosmotic flow and controlling the separation efficiency as well as the elution order. After extended investigation and optimisation of the separation and detection parameters glucose, fructose, tartaric acid, glycine, alanine, proline and sulphite could be determined.

References:

- [1] U. Backofen, W. Hoffmann, F.-M. Matysik, Capillary batch injection analysis: a novel approach for analyzing nanolitre samples, *Anal. Chim. Acta* 362 (1998) 213-220
- [2] T. Kappes, P. C. Hauser], Simplified amperometric detection for capillary electrophoresis, *Analyst* 124 (1999) 1035-1039
- [3] T. Kappes, P. C. Hauser, Portable capillary electrophoresis instrument with potentiometric detection, *Anal. Comm.* 35 (1998) 325-329

DETERMINATION OF TRACE LEVEL CHROMIUM(VI) BY FLOW INJECTION AMPEROMETRY AT GOLD MICROELECTRODES ARRAYS

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The quantitative determination of chromium concentration is of increasing interest, especially for environmental protection purposes. Its toxicity depends on the oxidation state, Cr(VI) being significantly more toxic than Cr(III). Soluble chromium species, especially Cr(VI) are used in many sectors of industry, e.g., electroplating, leather, paint, etc..

In the present work Cr(VI) as $\text{Cr}_2\text{O}_7^{2-}$ in sulfuric medium is determined by flow injection analysis (FIA) at a 24 gold microelectrodes array chip in the presence of Cr(III) and dissolved O_2 . FIA was carried out using an EG&G PAR 264 potentiostat and a PAR Model 150 Y-t recorder. A thin layer cell was constructed as described previously¹, the microelectrode array being pressed against an acrylic resin block. The block contains the inlet and outlet channels of the solution flow as well as an adaptation of the saturated Ag/AgCl miniaturized reference and auxiliary (stainless steel tube) electrodes positioned downstream. A 100 μL loop was employed in the sample injection. Cyclic voltammetry was performed using a similar design of the cell adapted for a higher volume of the solution.

The voltammetric response of Cr(VI) in a $5 \times 10^{-3} \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution shows a reduction wave under 0.50 V. The Cr(III) oxidation wave is observed in the same region as the gold one (above 0.70 V) while reduction of O_2 dissolved in the supporting electrolyte occurs at potentials under 0.10 V. Detection of Cr(VI) in the stream flow was performed at 0.20 V. A linear amperometric response to Cr(VI) in the 1×10^{-6} to $7 \times 10^{-6} \text{ mol L}^{-1}$ range was observed. The Cr(VI) detection limit for this experimental device is $2 \times 10^{-7} \text{ mol L}^{-1}$, assuming a three times signal-to-noise ratio.

The proposed flow injection method seems to be a promising procedure for routine determination of Cr(VI). Detection is simple and the concentration range is suitable for environmental samples. Moreover, it is indifferent to the presence of dissolved O_2 . The interference of other species in the flow analysis is presently under investigation.

Reference

1. Matos, R. C., Augelly, M. A., Pedrotti, J. J., Lago, C. L. and Angnes, L., *Electroanalysis*, 1998, **10**(13), 887-890.

Acknowledgements

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**DETERMINATION OF DIACETYL BY ADSORPTIVE STRIPPING
VOLTAMMETRY UNDER FLOW CONDITIONS AT THE HANGING MERCURY
DROP ELECTRODE WITHOUT OXYGEN REMOVAL**

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Diacetyl is a fragrant compound present in most food products obtained by fermentation. The amount of diacetyl in alcoholic beverages, such as beer or wine, must be strictly controlled because it can have an unpleasant effect on their organoleptic properties [1].

In this work a method was developed for the determination of diacetyl based on its rapid derivatization with o-phenylenediamine to form 2,3-dimethylquinoxaline and on the adsorptive stripping voltammetric determination of the quinoxaline using a HMDE flow cell. If a square wave voltammetric scan with a high frequency (higher than 100 Hz) is used, there is a significant increase in the ratio of the current due to the reduction of the adsorbed quinoxaline to the current due to the oxygen reduction, allowing the determination of the adsorbed compound without interference of oxygen.

The voltammetric flow cell was adapted from the one developed by L. R. Taylor [2] and was used as the detector of a basic FIA system, which also includes a peristaltic pump to deliver the supporting electrolyte and an injection valve to inject the sample in the flowing stream. The voltammetric scan is performed under flow conditions and the reproducibility and repeatability of the system are very good. A linear calibration range between 1×10^{-8} M and 1×10^{-5} M was obtained with standard solutions of diacetyl, with slightly different ranges being found for real samples. Up to 15 samples can be analysed per hour with a good precision (RSD < 2%).

References

1. M. Yamaguchi, J. Ishida, Z. Xuan-Xuan, M. Nakamura, T. Yoshitake, J. Liq. Chromatogr., 17, 203 (1994).
2. L. R. Taylor, Chemtech, 38 (1994).

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DETERMINATION OF CITRIC ACID IN SOFT DRINKS USING A POTENTIOMETRIC FLOW INJECTION SYSTEM

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Citric acid is of fundamental importance to living animals and plants. It is directly responsible for the production of energy by means of the Krebs cycle in addition to being determinant in several processes such as the metabolism of fatty acids, carbohydrates and certain amino-acids. Since this is an innocuous substance it is used in food industry as antibacterial agent and additive for pH control (1).

Several analytical methods such as electrochemical, spectrophotometric and chromatographic have been proposed for the determination of citric acid. Nevertheless, these feature an elaborate and time-consuming sample preparation being therefore unattractive for high frequency determinations.

Automated systems based on flow injection analysis (FIA) have been used for citrate determination. Some works resort to enzymatic reactions, either using citrate lyase and malate dehydrogenase, in which the reduction of NADH is determined by spectrophotometry, or citrate lyase, oxaloacetate decarboxylase and pyruvate oxidase that produce H_2O_2 which is determined by amperometry. Other FIA systems developed without enzymatic reactions use spectrophotometry as detection procedure or chemiluminescence.

The present work describes the development of a simple and inexpensive potentiometric FIA system based on the complexation of citrate ion with copper (II) ion. This determination is carried out indirectly by means of assaying the free copper concentration with a tubular shaped electrode sensitive to this ion. The samples being injected without prior treatment were adjusted to the analysis conditions inside of the FIA system.

Linear relationships between the potential and log concentrations of citric in the range of 1×10^{-3} - 1×10^{-2} mol/L were attained. Reproducibility was determined by assessing the relative standard deviation for ten replicate injections of different soft drinks, which varied from 1.2 to 3.0%.

The results provided by the automated system were compared to those of an enzymatic conventional method used for the analysis of citric acid in foodstuff and a relative deviation less than 4.0% was found. Recovery trials that presented values ranging from 97.0 to 101.0% were also performed. The system proposed allows a sampling frequency of 60 samples/h.

References:

- 1 - Plantá M., Lázaro F., Puchades R., Maquieira A. (1993). *Analyst*, **118**, 1193;
- 2 - UV-method for determination of citric acid in foodstuffs (1997), Boehringer Mannheim, Mannheim, .
Cat. No. 139076.

COMPARISON OF CONTINUOUS FLOW *VERSUS* FLOW INJECTION ELECTROPOLYMERIZATION OF CONDUCTING POLYPYRROLE FILMS IN THE PREPARATION OF GLUCOSE BIOSENSORS

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The electrochemical polymerization of conducting polypyrrole films has been carried out in a flow system considering two approaches: i) continuous flow electropolymerization, in which the electrolyte solution containing the monomer and the enzyme is continuously circulated through the thin-layer detection cell, and ii) flow-injection electropolymerization, by injecting a plug of the monomer+enzyme solution in the electrolyte carrier solution.

Conducting polymers do not exhibit a self-limited growth like occurs with non-conducting polymers (e.g. poly(*o*-phenylenediamine)), and they show a continuous growth whereas the monomer is available in the medium. The thickness and formation of this kind of polymers can be adequately controlled by combining typical parameters used in a batch system (e.g. concentration of the monomer, electrolyte composition, electrolysis time, applied potential) with other parameters related with a flow system (e.g. solution flow rate and detection cell and injection volumes).

The flow-injection electrosynthesis alternative for this kind of polymers gives a more complex situation than with a non-conducting polymer synthesis owing to the electrolysis time should be correlated with the dynamic parameters in order to discriminate between the charge involved in electropolymerization and the charge due to the overoxidation process, which takes place when the injected monomer has been consumed in the detection cell.

The same flow system where the electropolymerization takes place is subsequently used for the flow injection determination of glucose. The biosensors obtained by the two electrosynthesis alternatives are compared in terms of the flow scheme, reproducibility of the procedure, preparation costs (e.g. consumption of reactants), film permeation, sensitivity, and efficacy of the detection of the enzymatically generated hydrogen peroxide.

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ELECTROCATALYTIC FLOW DETECTION OF SOME S-CONTAINING COMPOUNDS ON METALLOPHthalOCYANINE MODIFIED ELECTRODES

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Voltammetry on the chemically modified electrodes (CME) is one of the perspective direction of electroanalytical chemistry. Specific properties of CME such as wide determination region, high sensitivity, selectivity and stability, simple preparation method allow to use them in flow analysis. At present, CME with electron transfers attract considerable interest. Usually electrocatalytic properties of these electrodes are investigated in batch and flowing solutions as well. As known voltammetric determination of sulfhydryl and thiocarbonyl compounds is troubled owing to high overvoltages at the solid electrodes. The overvoltage effect can be reduced with the help of redox-mediators involved in solution or electrode composition. It was established that electrodes modified by metallophthalocyanines (MPc) gives electrocatalytic response during electrooxidation of cysteine, thiourea and carbathion. The latter is a dithiocarbamate pesticide and its molecule possesses both groups $>C=S$ and $-SH$. Increasing of peak current and reducing of overvoltage effects were observed during electrooxidation of these compounds on CME. The electrode reaction includes electrochemical process of phthalocyanine metal (II) oxidation up to phthalocyanine metal (III) on electrode surface accompanied by substrate oxidation in solution. Electrocatalytic response was registered in the potential range of MPc oxidation. The best results were obtained on the CME based on CoPc and FePc. These CME were used as electrochemical detectors in flow systems. In order to obtain working conditions of flow analysis the relationships between electrocatalytic current and hydrodynamic parameters were studied. The detector response was evaluated with regard to flowing rate (u), applied potential (E) and injection volume (v). FIA conditions: $\Delta = 0,80$ V vs Ag/AgCl, $u = 3$ mL/min, $v = 800$ mL. In this case the electrocatalytic response is fast, linear and reproducible. Linear concentration relationship is observed in the range $1 \times 10^{-3} - 1 \times 10^{-7}$ mol/L. Productivity of FIA ~ 60 sample per hour.

BHT QUANTIFICATION BY HPLC WITH A POLYMER MODIFIED ELECTRODE DETERMINATION

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The use of antioxidants like butyl-hydroxy-toluene (BHT) in vegetable oils is especially widespread. Different methods have been described for BHT quantification including colorimetric methods, UV-HPLC, TLC or GC but only few electrochemical determinations were reported, probably due to the fact that phenolic compounds builds up an isolating layer over the electrode surface when they are oxidized. Phenol/formaldehyde polymer modified electrode has proved to avoid this poisoning allowing to obtain, in some cases better responses than the polished ones.

The aim of this work is to provide an alternative methodology for BHT quantification in various comestible oils by HPLC with amperometric determination, using a phenol/formaldehyde modified glassy carbon electrode. Different oil samples (corn, olive and sunflower) were analyzed with a simple extraction and dilution step. An isocratic (5% acetic acid, 15% isopropyl alcohol, 80% acetonitrile) run was performed with a C_{18} column using 1.00×10^{-2} M tetraethylammonium perchlorate as supporting electrolyte. The electrochemical cell consists of a stainless steel auxiliary electrode block with a 51 μm thick TG-2M teflon cell gasket and a Ag/AgCl/NaCl 3M reference electrode.

The effect of flow rate, amount of deposited polymer and working potential was tested in order to make the system optimization. Higher responses were obtained at lower flow rates but the best compromise between sensitivity and sampling rate was achieved at 1 mLmin^{-1} . Response vs working potential profiles showed a S-shaped curve with a plateau at 600 mV. Better signal/noise relations were found at 700 mV selecting this value as working potential. Detection limit, taken as three times the standard deviation of the blank signal, was 5.00×10^{-8} M.

The results were compared with those performed using UV detectors. In every case a good agreement between the two methods was obtained, being the difference of approximately 5%.

ELECTROCHEMICAL DETECTION FOR CAPILLARY ELECTROPHORESIS WITH CO-AXIS DISK ELECTRODES

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Due to its ability to provide extremely high separation efficiency, capillary electrophoresis (CE) has become popular analytical technique in the past decade. Among the more promising high sensitivity detection approaches for CE are electrochemical (EC) techniques. As the measurement is independent of path length, amperometric method has been naturally compatible with detection in a very narrow capillary with high inherent sensitivity. However, in order for the significant potential of EC detection to be realized in practice, a suitable electrode must be employed to use micro-size electrodes with simple fabrication and make electrode-capillary alignment easier to maintain both during an electrophoresis run and from run to run.

The design and characterization of a co-axis wall-jet electrochemical detector have been described for CE detection, which allows the use of normal size working electrode and accounting electrode together onto the outlet of capillary. In this approach, disk-shaped electrodes consisting of a metal wire of the desired dimensions or carbon-fibers by centrally inserting into a noble metal tubing serving as working electrode and accounting electrode respectively with only their surface cross the end-outlet of the capillary. The electrode-capillary alignment was simply configured by direct conjunction of electrodes and separation capillary through a positioning quartz tube outside the capillary. The detection was carried out in the same solution reservoir that contains the grounding electrode for the CE instrument.

The demonstration of the electrodes was carried out for the detection of amino acids and environmental sample of phenols by using copper as working electrode. Separation were performed on 60cm length of fused silica capillary with 25 μ m id and 375 μ m od. The electrophoresis medium was always 0.10M NaOH. Sample injection was carried out by electromigration by applying a potential of 10kV to the sample solution for the duration of 5s resulting injection volume about 1nL, and then run at 20kV. The results showed that all standard samples gave an increase in anodic current between +0.4 and +0.9V vs Ag/AgCl by cyclic voltametry. For the application of environmental samples, it gave out well quantitative determination.

Poster Contributions

Session F

PRESSURE MODULATION, A NEW TECHNIQUE FOR THE ELECTROCHEMICAL DETERMINATION OF ADSORPTION AND REACTION VOLUMES

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So far it is very difficult to determine reaction and adsorption volumes since there is a need for pressures up to $5 \cdot 10^9$ Pa, which is experimentally difficult to handle. With this new technique pressure in the electrochemical cell is modulated in a range of 10^5 Pa. This leads to a modulation of the equilibrium constant and subsequently to a ac current of the same frequency which can easily be detected with the lock in technique.

The adsorption volume ΔV^{ad} , derived from the Henry adsorption isotherm, can be expressed as:

$$\Delta V^{\text{ad}} = - \frac{I_A RT}{p_A \omega n F \Gamma}$$

with the ac current amplitude I_A , the pressure amplitude p_A , the angular frequency ω and the coverage Γ .

We have investigated the hydrogen adsorption at a platinum electrode in sulphuric acid with an addition of iron (II) and (III) as the referenz system. Further more we have examined the hydrogen adsorption at a platinum electrode in sulphuric acid using a platinum / oxygen referenz electrode.

Assuming that the double layer charge is independent of the pressure we get a value of $25 \text{ cm}^3/\text{mol}$ for the reaction volume of iron (II) / (III) which agrees well with the value obtained with high pressure measurements [1]. For the adsorption volume of the hydrogen adsorption we get $10 \text{ cm}^3/\text{mol}$.

This method not only simplifies the determination of reaction and adsorption volumes, but should also be applicable to the determination of activation volumes.

References:

- [1] R. Kaus, Ph.D. thesis, University of Erlangen-Nürnberg, Germany, (1978)
- [2] R. van Eldik, T. Asano, J. le Noble, Chem. Rev. **89** (1989) 549

A POLAROGRAPHIC APPROACH TO THE STUDY OF HETEROGENEITY IN HEAVY METAL- HUMIC MATTER SYSTEMS

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Complexation of metal ions by humic matter (HM) has become an important topic in environmental studies because its understanding is closely related to the metal bioavailability toxicity and mobility in natural systems [1].

Electrochemical techniques are outstanding in speciation studies of natural samples mainly due to its unbeatable detection limits and signal dependence on the identity of the species. Then, it is possible to obtain direct speciation estimations at the low concentration levels of some natural samples. However, the interpretation of natural sample signals is severely hindered by several occurring phenomena, such as electrodic adsorption, simultaneous presence of different kind of ligands, heterogeneity, lack of ligand excess, ... Up to now, most of the work concerning labile speciation studies has been done in conditions of a large excess of ligands, in which homogeneous and independent complexation can be assumed.

In this work, the outlined experimental methodology, based on a recently developed voltammetric model [2], could calculate the binding curve from experimental measurements of normalised limiting current at different values of total ligand and total metal concentrations for labile heterogeneous complexes. This methodology involves the ligand characterisation by means of a potentiometric acid-base titration, checking out some voltammetric tests on reversibility and lability, and voltammetric titrations from which eventually the speciation information will be drawn. Once the binding curve is obtained, standard analytical methods found in the literature [3] can be applied to render a proper description of the heterogeneity of the sample. The system studied was the Cd(II) + fulvic acid at fixed values of ionic strength and pH, due to the fact that it has been extensively studied as a model of heterogeneous interactions between the metal ion and fulvic acids.

References

- [1] Tessier, A.; Turner, D.R. (Eds.), *Metal Speciation and Bioavailability in Aquatic Systems*, Wiley, New York, 1995.
- [2] Garcés, J.L.; Mas, F.; Cecília, J.; Galceran, J.; Puy, J.; Salvador, J.; J. Submitted to *J. Electroanal. Chem.*
- [3] Van Riemsdijk, W.H.; Koopal, L.K. *Environmental Particles*. Vol 1. Buffle, J.; Van Leeuwen, H.P. (Eds.), Lewis Publishers. Michigan, 1992. Chapter 12.

THE AAS, ICP-MS AND ELECTROCHEMICAL DETERMINATIONS OF ZINC IN SELECTED PHARMACEUTICAL PREPARATIONS

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Zinc is one of the microelements indispensable for correct functioning of living organisms. As a constituent or activator of enzymes, zinc participates in protein and carbohydrate metabolism. Living organisms have been found to contain 18 enzymes containing zinc and 14 enzymes activated by zinc ions. Zinc is necessary in bone growth and particularly indispensable in the early development and growth stages. When combined with the molecule of insulin, zinc protracts the action of insulin and stimulates the activity of vitamin A stored in the liver. Daily requirements for adults have been established at 15 mg. Zinc is delivered primarily with food, but absorption of zinc by the body varies with the quality of food and interactions of zinc with concomitant elements. To alleviate zinc deficiencies in food, there are numerous supplementing preparations available on the pharmaceutical market. These are mostly multimineral and multivitamin preparations provided in the form of tablets, recommended for prophylaxis, and also preparations to be parenterally supplied in the case of manifest microelement deficiency. On the other hand, the inorganic zinc salts applied externally act as constrictants and they accelerate healing of wounds, and especially dermal deficit.

Controlling of elements content in drugs is indispensable for drug quality evaluation. Zinc was selected for study because zinc contents in drugs span a wide range. Numerous multi-mineral preparations used as nutritional supplements to make up for the microelemental deficiencies in humans and animals, contain less than 0.001% of zinc, *i.e.*, trace amounts of zinc. On the other hand, external application drugs such as ointments and suppositories usually contain more than 0.1% of zinc. Zinc was determined out in Technilab's "Hemcort HC" ointments and suppositories, in Nattermann's "Dolovit Multimineral" tablets, and in Richter Pharma's "Minerasol" parenteral veterinary fluid. These preparations were selected for investigation not only in view of differentiated zinc contents, but also because of the various drug forms and various procedures involved in sample preparation procedures. The tablets were dissolved with the aid of microwave energy, the ointment and suppositories were extracted, and the parenteral fluid was diluted with water or with an aqueous 1% nitric acid. Graphite-furnace atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), adsorptive stripping voltammetry (AdSV), square-wave voltammetry (SWV), and differential pulse polarography (DPP) were used for the determinations.

Zinc was determined within concentration ranges of 20-40 ppb, 0.5-20 ppb, and 10-50 ppb by AAS, ICP-MS and AdSV, respectively. In the AAS and ICP-MS, zinc recoveries were contained within the limits of 101.8-114.2% and 111.0-114.2%, respectively. The errors of determination (RSD) were 3.37-5.74% in AAS, 0.28-4.47% in ICP-MS and 0.19-2.50% in the electrochemical method. In view of the lack of certified reference materials, the use of complementary analytical methods has made it possible to verify the results obtained and to fully validate the methods developed.

THE VOLTAMMETRIC OXIDATION OF HALOGENOANILINES IN ACETONITRILE SOLVENT

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The voltammetric oxidation of p-substituted aniline derivatives is a well established dimerisation reaction which has been elucidated by J. Bacon and R.N. Adams, in aqueous media.¹ In the past few years, systematic investigations are in progress, in order to throw light on the oxidation of these compounds in aprotic solvent like acetonitrile. The ultramicro electrodes and fast polarisation gave the possibility to show direct evidence for the primary oxidation product, the radical cation, which has an extremely short lifetime even in aprotic media. By using wide range of polarisation rate gave the chance to give detailed mechanistic description of the dimerisation reaction of the radical, and the digital simulation of fast CV curves gave the opportunity to describe the dimerisation mechanism in details.^{2,3} In case of p-anisidine, a radical-substrate type dimerisation was found.² In cases of p-chloro- and -bromo-anilines however a complex radical-radical dimerisation exist.³ The classical voltammetric study and controlled potential electrolysis results, isolation of products, and their analysis by mass spectrometry showed a new element in the oxidation of halogeno-anilines. It is proved that at the radical dimerisation the lost halide ion participates actively in the electro oxidation. By taking the CV curves of Cl^- , Br^- and I^- in form of their n-TBA⁺-salts, these halide ions can be oxidised at coinciding or lower positive potential values, compared to the substrates. This way the radical dimerisation is not the single main follow up reaction, but one must take into consideration the parallel oxidation of the corresponding halide ion to elementary halogen, which substitute the substrate and dimer as well, in different degree. The role of this quite new result in the voltammetric oxidation of mono, di, and trihalogeno-aniline substrates is discussed in details. The model substrates studied: p-, 2-4 di-, 2-4-6 trichloro, bromo, and iodoanilines.

References

- 1/ J. Bacon, R.N. Adams: J. Am. Chem. Soc. 90 (1968) 6596
- 2/ P. Simon, G. Farsang, C. Amatore: J. Electroanal. Chem. 435 (1997) 165
- 3/ C. Amatore, G. Farsang, E. Maisonhaute, P. Simon: J. Electroanal. Chem. 462(1999) 55

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**SOLID-STATE ELECTROCHEMICAL, X-RAY AND SPECTROSCOPIC
CHARACTERIZATION OF MIXED CRYSTALS OF IRON-COPPER
HEXACYANOFERRATES**

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Copper and iron hexacyanoferrate form a continuous series of mixed crystals, which have been studied by solid state electrochemistry, x-ray powder diffraction, IR and ESR spectroscopy. All methods unambiguously prove the formation of mixed crystals. The results show the different capabilities of these techniques to study mixed crystal systems. Esp. in the case of poor crystallinity and strongly magnetically interacting metal ions, voltammetry of immobilized microparticles offers a powerful tool for the determination of the composition of mixed crystals.

**DETERMINATION OF DIFFUSION COEFFICIENT OF SODIUM
DITHIONITE AND MECHANISM OF OXIDATION
REACTION IN ALKALINE SOLUTION**

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The electrochemical behavior of sodium dithionite at a platinum electrode has been investigated in alkaline solutions using cyclic voltammetry at a rotating disc electrode.

Two oxidation waves were observed. Using their limiting current, it has been found that the first oxidation step is controlled by the rate of mass transport, while the second is not purely controlled by transport phenomena. From the ratio of the limiting currents of both oxidation waves, and by extrapolation to small rotation rates of the electrode, it has been determined that sulfite is formed as stable intermediate species and sulfate as final product of the oxidation of sodium dithionite. The diffusion coefficient of sodium dithionite has been calculated from the limiting current of the first wave of the oxidation reaction.

From the obtained results, it is also advisable to make use of the first oxidation reaction for analytical purposes (eg. control of the concentration of sodium dithionite).

A mechanism of the oxidation reaction has been proposed at a platinum electrode in solutions of sodium dithionite of pH 12 to 13.

NEAR CRITICAL AND SUPER CRITICAL FLUIDS IN ELECTROCHEMICAL SENSORS

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Electrochemical sensors with directly heated electrodes ("Hot-Wire" or "Hot-Layer" electrodes, see [1] and references cited there) can generate their own reaction medium in form of a thin layer of super heated, near critical or even super critical fluid. This way, in an open system without walls, extreme reaction conditions can be established that may be utilised for sensing of slowly reacting species in the environment, in flowing streams, and at other remote places.

To reach the supercritical state, a solvent must have not just critical temperature, but also the appropriate critical pressure. This can be accomplished in an open system only by extremely fast temperature rise. Direct Joulean heating, as common in Hot-Wire electrodes, is adequate to generate such extremely steep temperature jumps.

In contrast to every existing solvent, water has extraordinary high critical parameters and requires special effort to be driven into super critical state. On the other hand, near to this point, solvent characteristics of water can be modified dramatically with the consequence that a great variety of quite different reaction types might be brought about when the solvent properties are "scanned" this way.

Numerical calculations and experimental results demonstrate the existence of a thin supercritical water layer near to the surface of a heated platinum electrode wire. This layer persists only for short life time just sufficient to obtain electrochemical signals. Repeated cycling with very short, intense heat pulses became the basis of a special near critical variant of "Temperature Pulse Voltammetry" (TPV, see [2]).

Measurements are important not only for analytical sensors, but can provide valuable information about processes occurring in sonoelectrochemistry and in super critical water oxidation.

References

1. P. Gründler, A. Kirbs, *Electroanalysis* 11(1999)223
2. T. Voß, P. Gründler, A. Kirbs, G.-U. Flechsig, *Electrochem. Commun.* 1(1999)383

**CYCLIC VOLTAMMETRY AND QUARTZ CRYSTAL MICROBALANCE
ELECTROCHEMICAL
STUDIES ON THIOSALICYLIC ACID AND DITHIODIBENZOIC ACID**

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Thiosalicylic acid belongs to the group of nonsteroidal antiinflammatory drugs. It also acts as an analgesic, antipyretic and antirheumatic. Thiosalicylic acid derivatives have been shown to exhibit a twofold activity: first of all they inhibit subcortical cerebral centers and they also inhibit perception of pain in sensory endings; additionally, in inflammatory states, they reduce pain by reducing edema. The mechanism of action of salicylates has been recognized only recently, involving inhibiting the biosynthesis and release of endogenous prostaglandins and their precursors from tissues. These compounds are readily absorbed from the alimentary tract, partly in the stomach, primarily in the upper portion of small intestine. They penetrate easily into tissue and body fluids, among other things, through the placenta to fetal tissues. They are slowly removed together with urine (as little as 10% in the unchanged condition) and hence are likely to accumulate in the body.

Cyclic voltammetry (CV) and electrochemical quartz crystal microbalance (EQCM) were used to study the behavior of thiosalicylic acid (KTS) and dithiodibenzoic acid (DTDB) at the controlled-growth mercury drop electrode (CGMDE), at the gold electrode, and at the carbon electrode. The CV method was used to study peak current intensities and peak potentials in relation to pH of the solution, to electrode polarization rate and to the concentration of the analyte. Optimum measurement parameters were established and stock solutions developed. The electrode activity was found to be primarily due to the oxidation of the sulhydryl group. The currents observed are diffusion currents. Electrochemical studies on complexes of KTS with Cu(II) were undertaken at varying constituent proportions and the cathodic peak was found to rise by *ca.* 70% whereby the sensitivity of the determination was considerably increased.

The EQCM method allowed to establish that, as KTS is oxidized, the electrode slightly gains in weight (*ca.* 80 ng). As DTDB is reduced, the electrode slightly loses in weight (*ca.* 40 ng). Studies on the equimolecular KTS-Cu(II) complex showed the electrode to gain about 125 ng more in weight than in the solutions containing KTS alone, a fact evidencing for the formation of the complex and for its deposition on the electrode surface. In the solution containing Cu(II) ions alone in 0.3 mol/dm³ HNO₃, the electrode weight gain was ten times as high, about 1550 ng.

A procedure was developed to determine KTS and DTDB in the substance by the CV method. Statistical evaluation of data showed the results to be characterized by good accuracy and precision (RSD 0.80% and 0.61%, respectively).

APPLICATION OF ELECTROCHEMICAL METHODS FOR THE INTERACTIONS STUDY OF SOME SYNTHETIC ORGANIC MATTERS WITH CLAY MINERALS

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Clay minerals occur in the form of colloidal dispersion state in aqueous systems while a more aggregated state characterizes their deposits in sediments and soils. In the presence of synthetic small amphiphilic surfactant molecules or (un)ionized polymers, the clay minerals surfaces are modified which not only influences these different states but also their binding capacities to nutrient molecules and pollutants. Different electrochemical methods were thus applied to characterize and understand the interactions of these organic matters with clay minerals aqueous dispersions and films.

The *tensammetric method* was used to directly measure the concentration of a cationic surfactant in equilibrium with very dilute suspensions of montmorillonite, a negatively charged clay mineral [1]. *Microelectrophoretic measurements* along the double-step binding isotherm also allow the formation of a surfactant molecule bilayer to be observed.

The microelectrophoretic method was also used to investigate the molecular weight dependence of water-soluble nonionic polymer polyvinylpyrrolidone (PVP) adsorption behaviour on clay minerals dispersions. The results from adsorption isotherms are discussed with the electrokinetic layer extension due to adsorbed PVP measured from the zeta potential of the clay minerals particles [2].

Effects of water-soluble polymers on the hexacyanoferrate (III) transport through coated montmorillonite clay film at a platinum electrode were also studied with the *cyclic voltammetric method* [3]. Arrangements of montmorillonite particles in film are discussed from a relationship between the diffusive transport, a shape factor which includes the orientations and axial ratios of particles, and the clay film effective porosity obtained from sedimentation volume measurements.

References

- [1] J.-M. Séquaris, *Langmuir*, **1997**, *13*, 653
- [2] J.-M. Séquaris, F. Baßmann, A. Hild, H.D. Narres, M.J. Schwuger, *Colloids Surf. A* **1999**, *159*, 503
- [3] J.-M. Séquaris, *Langmuir*, **2000**, *16*, 1368

HEATED MERCURY FILM ELECTRODES ON IRIIDIUM AND CARBON BASIS

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Directly heated mercury film electrodes (MFEs) extend the operational capabilities of the hot layer technique to a wide range of electroanalytical systems. They abolish the restrictions of the metal electrodes (mainly gold and platinum layers and wires) used so far, which can only be applied for the determination of a limited number of metals - predominantly Pb, Bi, Hg, Cu and As. Both the general advantages - e.g. enhanced signal to noise ratios and the replacement of mechanical stirrers during deposition - and the theoretical resp. experimental fundamentals of heated electrodes have been published [1-3].

The heated iridium-based MFE was manufactured using sputtering techniques [4]. Iridium is an optimum metal substrate because of its very low solubility in mercury and good wettability. Compared to classic Ir-MFEs the surface of its heated counterpart is larger for constructional reasons. This requires the application of a more complicated mercury deposition procedure which is described in detail.

The heated carbon-based MFE was made by screen-printing. The screen-printing (thick film) microfabrication technology is commonly used for large-scale production of extremely inexpensive and highly reproducible electrochemical sensors. The electrode itself is easy to assemble, a sufficient supply can be build much faster.

The development procedures, the thermal and the electrochemical properties of both electrode types are described. Applications in the field of heavy metal determination are presented.

References

1. T. Zerihun and P. Gründler, *Journal of Electroanalytical Chemistry* **415** (1996), 85
2. P. Gründler, A. Kirbs and T. Zerihun, *Analyst* **121** (1996), 1805
3. P. Gründler, *Fresenius Journal of Analytical Chemistry* **362** (1996), 243
4. M. Jasinski, A. Kirbs, M. Schmehl and P. Gründler, *Electrochemistry Communications* **1** (1999), 46

ANALYTICAL INVESTIGATIONS OF THE NEW ORGANIC PLATINUM(IV) DERIVATIVE

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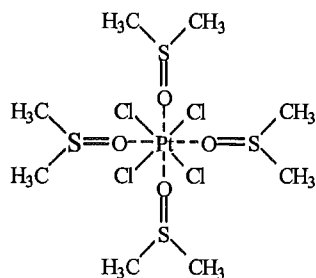
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The aim of this work was to estimate: purity, contamination and structure of dimethylsulfoxide derivative of platinum(IV). To ascertain this purpose, we applied: reverse phase high performance liquid chromatography (RP-C18 HPLC), cyclic voltammetry (CV) on glassy carbon electrode, UV and IR spectrophotometry, mass spectrometry (MS), Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) and ^1H , ^{13}C NMR spectrometry.

In time course of HPLC analysis we registered spectrum of compound in its peak maximum (range 200-350 nm). Using HPLC method we confirmed also purity of investigated platinum(IV) derivative. Structure investigations included: IR spectroscopy in range 4000 cm^{-1} - 300 cm^{-1} , mass spectrum, ^1H , ^{13}C NMR spectrometry and estimation of platinum by ICP-MS $^{195}\text{Pt(IV)}$ isotope method. Using CV we stated that investigated derivative was reduced irreversibly on the carbon electrode giving two cathodic peaks by -1.210 V and -1.467 V, while hexachloroplatinic acid reduced by -0.580 V, -1.553 V and -1.659 V. We not observed the anode peak by +0.574 V, characteristic for hexachloroplatinic acid.

Dimethylsulfoxide platinum(IV) derivative was almost fully extractable from reaction environment to DMSO and gave sediment after partial evaporation of DMSO. It contained 43.4% of platinum.

Obtained results permits us to establish the tentative structure of this compound as follow:



MEASURING ELECTRIC RESISTIVITY OF SOLID INSULATING MATERIALS BY MEANS OF LOW FREQUENCY DIELECTRIC SPECTROSCOPY

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Plastics, which are used as insulating materials in electric devices have to be qualified by passing a large number of material tests. Among other properties, electric volume and surface resistivity are determined. To do so, the present test method (International Standard IEC 60093) demands the evaluation of a time dependent value using direct voltage. Usually this time-domain value of electric resistivity is recorded 1 minute after electrification.

However, measuring electric volume or surface resistivity with direct voltage methods is not easy when authentic values are expected. To gain accurate values it is necessary to be aware of polarisation effects by shorting the probe and measuring discharge current until it is constant. Thus to begin with the real resistivity measurement requires a lot of time. Even if a high standard on care is taken by carrying out this tests, the reproducibility of measured values often is unsatisfactory. In practise deviations of one order of magnitude are not unusual.

Nevertheless, volume and surface resistivity can be determined in an other way: By measuring the specimen's capacity and dielectric dissipation factor over a broad frequency band with alternating voltage (dielectric spectroscopy) and applying a Fourier transform to the obtained values it is possible to calculate a time domain value (e.g. 1-minute-value).

Because of measuring with alternating voltage, polarisation which may exist before electrification does not affect the measurement. Therefore the obtained resistance/resistivity values are more reproducible. Further on the technique has the advantage of obtaining permittivity and dissipation factor (according to IEC 60250) simultaneously with the volume resistance measurement because of the identical electrode geometry for this case.

On the other hand the alternating voltage method has to be discussed and validated carefully, especially in reference to the influence of non-linear material behaviour. As applying a Fourier transform to the obtained dielectric spectra needs linearity, non-linear material behaviour (as shown by common insulating materials) has to be considered.

For validation of the alternating voltage test method comparison tests had been carried out. A good correspondence to values obtained by direct voltage was archived, and the reproducibility of measurement was found to be increased. The influence of non-linear effects in material behaviour on the results also has been considered. Last but not least recommendations are given for increasing performance and efficiency in laboratory.

COMPETITIVE POTENTIAL OF ELECTROANALYTICAL OVER OTHER METHODS IN SURFACTANT ANALYSIS

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Competitive potential of electroanalytical methods over chromatographic, spectrophotometric, mass spectrometry and classical methods in surfactant determination concerning: a. application range, b. cost and availability of apparatus, c. complexity of required preliminary separation stage, is critically analysed. Potentiometric titration using a surfactant-selective electrode is advantageous over classical two-phase titration in the determination of ionic surfactants within a milligramme-per-litre concentration range. Potentiometric titration with tetraphenylborate is also, in some aspects, advantageous over the classical BiAS method in non-ionic surfactants (NS) determination. The indirect tensammetric method (ITM) is advantageous over any recent version of BiAS in terms of NS determination in raw and treated sewage, and especially in surface water, as well as analytical control in biodegradation tests. ITM provides several unique analytical options (unlike other methods): i. determination of NS adsorbed on particles of surface water [1], ii. determination of NS adsorbed on alive activated sludge, iii. determination of NS in the presence of hydrocarbons [2], iv. determination of NS in tap water, v. determination of poly(ethylene glycols) [3], - the main by-product of NS biotransformation. So far, electroanalytical methods are not advantageous over other methods in anionic and cationic surfactants determination over the submilligramme-per-litre range. Lack of standards, reference materials as well as established interlaboratory experiments are serious problems in comparison of different methods for surfactant determination.

References

1. B.Wyrwas, A.Szymanski and Z.Lukaszewski, *Anal.Chim.Acta*, 331(1996)131
2. A.Szymanski and Z.Lukaszewski, *Talanta*, 47(1998)325
3. A.Szymanski and Z.Lukaszewski, *Analyst*, 121(1996)1897

ELECTROANALYSIS OF HYDROTHERMALY SYNTHESISED PRUSSIAN BLUE

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High pressure hydrothermal synthesis is a new methode for the recrystallisation of Prussian blue and analoguos compounds. With this technique for the first time it was possible to obtain potassium containing single crystals of Prussian blue. The real structure of these crystals was studied by X-ray powder diffraction, SEM and TEM. Electrochemical investigations are made in solutions containing H^+ , Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Tl^+ and NH_4^+ . Obviously the real structure plays an important role in the insertion electrochemistry of these compounds. The new Prussian blue samples differ in their electrochemical behaviour from samples synthesised under normal conditions (so called colloidal Prussian blue). As Prussian blue and analogous compounds are applicable as ion selective materials in composite electrodes it seems to be very interesting, that better crystalised samples show a higher selectivity for potassium as colloidal samples.

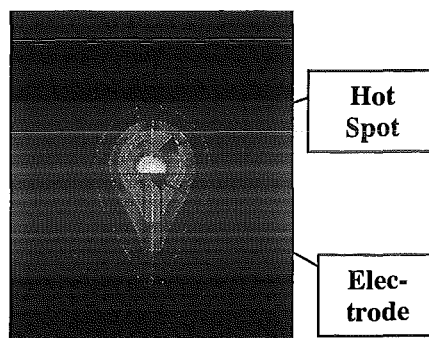
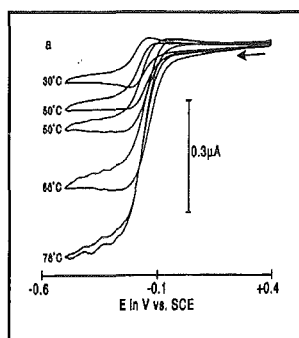
MICROWAVE ACTIVATION OF ELECTROCHEMICAL PROCESSES

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Microwave activation of chemical and especially heterogeneous chemical processes is a very rapidly developing area of research [1]. The activation of electrochemical processes, both homogeneous and heterogeneous, by microwave radiation has become possible only very recently [2] and offers a new tool for the study of microwave activation as well as new areas of applications. Microwave radiation is known to interact with condensed materials with dielectric loss and interfaces and may therefore be employed to directly activate an electrochemical system.

Below cyclic voltammograms for the reduction of $\text{Ru}(\text{NH}_3)_6^{3+}$ in aqueous 0.1 M KCl at a 100 μm diameter platinum electrode are shown in the absence and in the presence of microwave radiation. In first approximation effects can be understood in terms of localised heating and the formation of a 'hot spot' in the vicinity of the electrode surface. Computer simulation confirm heating with a considerable thermal gradient *within* the diffusion layer.



- [1] See for example 'Microwave-Enhanced Chemistry', H.M. Kingston, S.J. Haswell, Eds., American Chemical Society, Washington, 1997.
- [2] R.G. Compton, B.A. Coles, F. Marken, Chem.Comm., 1998, 2595.

**THE INTERACTION OF PRUSSIAN BLUE AND DISSOLVED
HEXACYANOFERRATE IONS WITH GOETHITE (α -FeOOH) STUDIED TO
ASSESS THE CHEMICAL STABILITY AND PHYSICAL MOBILITY OF
PRUSSIAN BLUE
IN SOILS**

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Colloidal Prussian blue and truly dissolved hexacyanoferrate ions strongly interact with the surface of goethite (α -FeOOH) particles. Whereas Prussian blue is deposited on the surface of goethite as a solid phase with all typical properties of solid Prussian blue, the hexacyanoferrate ions form initially a layer of surface bond hexacyanoferrate ions, which exhibit properties intermediate between those of free hexacyanoferrate ions and hexacyanoferrate ions bond in Prussian blue. The products of interaction of goethite with Prussian blue and hexacyanoferrate ions were studied by voltammetry of immobilized microcrystals, by infrared spectrometry, VIS diffuse reflection spectrometry, transmission electron microscopy and ESR-spectroscopy. The kinetics of Prussian blue destruction was measured by solution VIS spectrometry and also by voltammetry of solid microcrystals. The remarkable stability of Prussian blue in soils can be explained by its strong adherence as a solid phase to iron oxides and oxide hydroxides in soils. This prevents the formation of soluble colloids of Prussian blue. It does not prevent the hydrolysis of Prussian blue to iron oxide hydroxides and hexacyanoferrate(II) ions at elevated pH which proceeds at almost the same rate as that of pure Prussian blue colloid. Even when this hydrolysis of Prussian blue occurs, it is the hexacyanoferrate(II) which is effectively adsorbed on the surface of iron oxide hydroxides, again decreasing the physical mobility of hexacyanoferrate.

CHRONO-VOLTAMPEROMETRY AS A METHOD OF METAL-METAL THIN FILM SYSTEMS INVESTIGATION

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In the present work the results of CHVA (chrono-voltamperometric) investigations of multistep electrochemical processing and interdiffusion in multilayer thin film structures are presented. Chrono-voltamperometry recording of basic electrochemical anodization parameters (anodization current density and forming voltage) variation and their first derivatives permit to determine the correlation between the kinetics of anodization and concentration depth profiles of multilayer anodic oxide thin film compositions. For each concentration region of electrochemical anodization (EA) profile the definite character of CHVA dependence corresponds. The transition from layer to layer at that being recorded, clearly.

Under investigations of interdiffusion in multilayer thin film compositions the CHVA method is not inferior to the method of electrical resistivity, but is much more illustrative in information volume.

Anodization kinetics of Ta (45 nm) on Al (1,0÷2,0μm) thin film composition was investigated. CHVA diagrams in conjunction with AES depth profiles have permitted to determine the sequence of anodic oxide film formation of combined composition. Low temperature character of CHVA measurements does't allow additional rearrangement of anions. As a result, the mechanism anodization of multilayer thin film composition may be investigated. In particular, it permits to determine presence or absence of the cation order alteration.

Under investigation of thermally stimulated diffusion in Ta/Al thin film system (layers thickness varied in a broad range) the formation conditions of a uniform continuous layer of intermetallic compound, which is an effective diffusion barrier, were determined. The influence of impurities on kinetics of new phase formation has been studied.

The results of this investigation will be find practical usage in the technology of microelectronic, optoelectronic devices and flat panel displays production.

DETERMINATION OF HYPERICIN IN VARIOUS BIOLOGICAL FLUIDS BY DIFFERENTIAL PULSE POLAROGRAPHIE

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Hypericum perforatum (*St. Johnswort*) as well as its medicinal preparations are used in the treatment of mild to moderately severe depressive disorders [1,2]. Extracts of *St. Johnswort* contain a spectrum of six major natural product groups: Naphthodianthrones (hypericines), acylphloroglucinols (e.g. hyperforin), flavonol glycosides, biflavones, proanthocyanidins and phenylpropanes [3].

For the analysis of hypericin in phytotherapeutic preparations a photometric procedure, chromatographic methods and an electrochemical analysis were suggested [4-6]. To determine hypericin in plasma and urine a HPLC method was applied [7].

The electrochemical characteristics of hypericin induced us to develop a differential pulse polarographic method for the determination of hypericin in biological fluids. To analyze hypericin in urine by DPP an extraction step with ethylacetate is necessary. The recovery of hypericin is 91.0 % with a standard deviation of $\pm 3,3$ %. The detection limit of quantitation is 500 ng/ml. The experimental details of the analysis of hypericin in biological fluids will be given in our presentation.

References

1. Volz, H. P., *Pharmacopsychiatr.* **30**, 72-76 (1997).
2. Linde, K., Ramirez, G., Mulrow, C. D., Pauls, A., Weidenhammer, W. and Melchart, D., *Brit. Med. J.* **313**, 253-258 (1996).
3. Erdelmeier, C. A. J., *Pharmacopsychiatr.* **31**, 2-6, (1998).
4. Schütt, H., Hölzl, J., *Pharmazie* **49**, 206-209 (1994).
5. Gaedcke, F., *Dtsch. Apoth. Ztg.* **137**, 117-121 (1997).
6. A. Michelitsch, B. Biza, M. Wurglics, M. Schubert-Zsilavec, A. Baumeister, W. Likussar, *Phytochem. Anal.*, 2000, **11** (1), 41-44
7. Liebes, L., Mazur, Y., Freeman, D., Lavie, D., Lavie, G., Kudler, N., Mendoza, S., Levin, B., Hochster, H., Meruelo, D., *Analytical Biochemistry* **195**, 77-85 (1991).

REMOVAL OF Cu^{2+} AND Cd^{2+} FROM AQUEOUS SOLUTIONS ONTO RETICULATED VITREOUS CARBON COATED ELECTRODES

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Environmental contamination by heavy metals is a widespread problem, with sources of pollution arising from industrial activities. These metals are of significant importance as they are non-biodegradable and once released in to the environment, they can only be diluted or transformed, not destroyed. The development of simple methods for the monitoring of heavy metals in aqueous samples is a relevant field of research. It must be emphasized that Cd^{2+} is one of the most toxic elements for animals and human beings⁽¹⁾.

In this connection, the removal of Cu^{2+} and Cd^{2+} ions from sulfuric solutions containing 12 ppm of Cu^{2+} and 2 ppm Cd^{2+} was investigated by using reticulated vitreous carbon (RVC) coated with polypyrrole. The modified electrodes were prepared by polymerization of pyrrol under potentiostatic conditions at 0.90Vecs, followed by a reduction process at -0.90Vecs for 30 minutes⁽²⁾. Solutions of Cu^{2+} or Cd^{2+} ions containing dissolved O_2 were placed in contact with the recovered electrodes alternatively at open circuit potentials (OCP) and at a potential of -0.40Vecs for Cu^{2+} and -0.60Vecs for Cd^{2+} . The spontaneous reaction between $\text{PPy}^{(0)}$ and Cu^{2+} shows an efficiency removal of about 83% in 90 min. In the case of Cd^{2+} at OCP the removal was negligible in the same experimental conditions. In the electrodeposition process, the Cu^{2+} concentration decay was about 94% while for Cd^{2+} it was lower in the same time interval. The concentration decay of Cd^{2+} was followed by stripping at a hanging mercury electrode while for Cu^{2+} a stripping voltametric method at a Pt ultramicroelectrode was employed⁽³⁾. Experiments aiming the exhaustive removal of these metals are under investigation in the laboratory.

References

- [1] Robles, L. C.; Aller, A. J., *Talanta*, 42 (1995) 1731.
- [2] Rajeshwar, K.; Ibañez, J. G.; Swain, G. M., *J. of Appl. Electrochem.*, 24 (1994) 1077.
- [3] Hasse, E. E. S.; Castagno, K. R. L.; Piatnicki, C. M. S.; Azambuja, D. S.; Selbach, V., *Can. J. of Anal. Sci. and Spectr.*, 43 (1998) 153-160.

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ELECTROANALYTICAL STUDING OF Ni_{51.24}Ti_{48.76} SHAPE MEMORY ALLOYS

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Hot-Isostatic Pressing (HIP) technique is used for preparing of NiTi shape memory alloys from pure powders. The microstructures and martensitic phenomena in this system of alloys are studied in a wide range of temperatures by using different analyses. Electroanalytical investigations of Ni_{51.24}Ti_{48.76} samples are conducted by classical four point method in argon-4%hydrogen atmosphere, in different heating regimes. Specific electrical resistivities in function of temperatures are obtained in the range of temperatures from 293 K till 1173 K, during heating/cooling of samples by different velocities in the interval from 3 K/min till 30 K/min. Also, specific electrical resistivities in function of heating time are obtained too, in the regime of heating samples at constant temperatures, during the same intervals of time. In this case, voltage changes are registered of each 200 seconds, during heating samples at constant temperatures in 30 minutes intervals, for each temperature in the range from 298.6 K to 826.7 K. Particular attention is paid to adiscussion mentioned results, and to a variety of anomalous effects, which are frequently called premartensitic phenomena, occur in the pharent phase at temperatures above $M_s=334.03$ K, obtained by calorimetric analyses. Some of our considerations will be reported here.

A CONDUCTANCE ELECTRIC STUDY OF PbO_2 PARTICLES IN THE ACID SOLUTION OF H_2SO_4 WITH THE PRESENCE OF THE ELECTRIC FIELD

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Since antimony has a wide application in the battery industry, its effect on the positive plate has been studied extensively [1;2]. Rand et al [3] and Arifiku et al .[4] determined the antimony in the corrosion layer. Rogachev et al. [5] established the influence of antimony on the corrosion rate for different operation modes of the lead/acid battery. Abul Azim and Ismail [6] studied the influence of Sb_2O_3 and As_2O_3 on the cycle life of positives plates. Maja et al. [7] established that the presence of antimony as a dopant in the PbO_2 increases the electrode capacity. Yeo et Johnson. [8] found that the presence of group V dopants (bismuth and arsenic) in the PbO_2 phase accelerates many reaction with oxygen transition. If the whole of the particle charge is not zero, the conductivity increases with increasing solution concentration. Once the equilibrium is reached, the ratio $\gamma/K < 1$, i.e., when the number of the ions in the dispersive medium increases and the thickness of the diffusive layer decreases. This non-charged PbO_2 particles and an excess of hydronium concentration causes a diminution of the conductivity and the polarisation degree [9]. This paper deals with the relation ship between the conductivity with agitation of PbO_2 , the different quantities of antimony, tin and arsenic, the different concentration of the acid solution of H_2SO_4 and the different values of the electric field. In order to obtain the good values of the conductivity with stirring of the particles of the lead dioxide in suspension in the electrolyte of the acid solution , it's necessary to found the appropriate values of the electric field, the good concentration of H_2SO_4 and the ideal quantities of antimony, tin and arsenic in the acid solution.

References:

1. K.Gibson, K.Peter and F.Wilson, in J.Thompson (ed.), Power Sources 8, Academic Press, London, 1980, p.565.
2. N.A.Hampson, S.Kelly and K.Peter, J.Appl. Electrochem., 10 (1980) 91, 261
3. D.Barrett, M.T.Frost, J.A.Hamilton, K.Harris, I.R.Harrowfield, J.F.Moresby and D.A.J.Rand, J.Electroanal.Chem., 118 (1981) 131
4. F.Arifuku, H.Yoneyama and H.Tamura, J.Appl.Electrochem., 9 (1979) 629, 635
5. T.Rogachev, G.Papazov and D.Pavlov, J.Power Sources, 10 (1983) 291
6. A.A.Abdul Azim and A.A.Ismail, J.Appl.Electrochem., 7 (1977) 119
7. A.Boggio, M.Maja and N.Penazzi, J.Power Sources, 9 (1983) 221
8. H.Yeo and D.C.Johnson, J.Electrochem. Soc., 134 (1987) 1973.
9. N.Saidi, H.Saidi, B.Saidani and S.P.Stoylov, J.Power Sources, 64 (1997) 61-64

NEW OBSERVATIONS IN HYDROGEN PERMEATION THROUGH PALLADIUM MEMBRANES

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The hydrogen permeation of steel, iron and many alloys is an important parameter for certain of their applications (enamelling, constructions). Most frequently used to study the hydrogen permeation is the electrochemical method developed by Devanathan and Stachurski [1]. Despite various investigations there is still no consensus regarding several topics of the method. Two points of discussion are: the use of a palladium coating on the input and/or output surface of the membrane and the determination of diffusion coefficients from the permeation measurements. A palladium coating at the output surface is needed to protect the membrane against oxidation. An oxide layer can be seen as a barrier for the hydrogen permeation. At the input surface a palladium coating stabilises atomic hydrogen. An important condition that needs to be fulfilled when diffusion coefficients are determined from these permeation experiments, is that the hydrogen transport through the membrane must be the rate determining step. For this reason the hydrogen permeation characteristics through a palladium membrane were investigated in this work. By variation of the input current and investigation of the pH and temperature dependency, it was possible to show that the diffusion of hydrogen through a palladium membrane controls the rate of the overall permeation experiment. The fulfilment of this condition allowed to deduce diffusion parameters like the diffusion coefficient of hydrogen in palladium. A high correlation with values in literature was obtained except for the breakthrough time method. A reason for the latter could not yet be found but it was proved that the explanation given by Devanathan and Stachurski can not be correct. The values obtained for the diffusion coefficient are rather small, which is an important conclusion concerning the use of palladium as protective coating for permeation experiments in steel and other materials.

Reference

1. Devanathan M. A. V., Stachurski Z., Proc. R. Soc. London, 270a (1962) 90

TOTAL ORGANIC CARBON (TOC) ANALYSIS BY A PHOTODEGRADATION BASED APPARATUS USING NANOCRYSTALLINE TiO_2 AS CATALYST.

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TOC analysis is generally based on the measure of the CO_2 formed in the degradation of organic compounds. CO_2 measure is generally realized by IR analysis and the decomposition is carried out chemically at high temperature. More recent systems use chemical photoassisted degradation combined with IR analysis.

Such systems are characterized by high costs and some instrumental complexity.

In this paper a simple and compact low cost apparatus is studied; it is based on the photocatalytic degradation of organic compounds on irradiated TiO_2 surface and on the measure of produced CO_2 by CO_2 sensor. The catalyst is suitably immobilized in a membrane in contact with the CO_2 electrode. The measure cell is thermostatable and allows to operate in flow.

TiO_2 photoactivity depends on its morphological form: anatase shows higher photoactivity than rutile. Besides, TiO_2 superficial area is of great importance, as the degradation happens thanks to the superficial interaction between light, TiO_2 and organic compounds; for this reason, nanocrystalline TiO_2 is studied. In addition, the effect of substrate concentration, flow rate, temperature, TiO_2 loading, total volume of substrate solution and geometry of the cell on the efficiency is investigated.

**CHRONOPOTENTIOMETRIC STUDY OF LACCASE CATALYSED OXIDATION
OF QUINHYDRONE MICROCRYSTALS IMMOBILISED ON A GOLD
ELECTRODE SURFACE AND OF THE OXIDATION OF A PHENOL
DERIVATISED GRAPHITE ELECTRODE SURFACE**

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Solid microcrystallin quinhydrone immobilised on the surface of a gold electrode was oxidised by oxygen under the catalytic action of the enzyme laccase. In a buffered medium, this enzymatic reaction was followed by chronopotentiometry monitoring the conversion of hydroquinone to quinone. From the potential time dependencies the degree of conversion versus time was calculated. The reaction exhibits an accelerating kinetics. A variation of the laccase concentration (activity) shows that there is a maximum rate at an activity of 0.023 U/ml. Further increase in activity leads to a pronounced decrease in reaction rate. When a graphite electrode is first oxidised by boiling nitric acid, then electrochemically reduced in an aqueous potassium nitrate solution, it contains phenolic surface groups. These surface groups can be aerobically oxidised under the influence of laccase and the reaction rate versus laccase activity curves resemble those for quinhydrone oxidation. These experiments prove that laccase can directly interact with a solid surface.

MODELLING OF SOLID-STATE VOLTAMMETRY OF IMMOBILIZED MICROCRYSTALS ASSUMING AN INITIATION OF THE ELECTROCHEMICAL REACTION AT A THREE-PHASE JUNCTION

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The electrochemical reduction of a solid compound characterized by a mixed ionic/electronic conductivity, immobilized on an electrode surface and in contact with an electrolyte solution has been studied theoretically. The uptake or expulsion of electrons and electrolyte cations

$$\text{Ox}_{\text{solid}} + e^-_{\text{electrode}} + \text{C}^+_{\text{solution}} \rightleftharpoons \text{RedC}_{\text{solid}}$$

is coupled to maintain electroneutrality and is assumed to obey Fick's law of diffusion. Starting with the fully oxidized species, the simultaneous uptake of cations and electrons will be possible at the three-phase junction only, where electrode, solid and electrolyte solution meet. From this point, electrons and cations diffuse perpendicularly into the crystal lattice. The reaction zone grows due to the formation of the electronically and ionically conducting reduced product. Two and three-dimensional models have been utilized to simulate the diffusion and the current flow in response to an applied potential step. The resulting chronoamperometric curves have been analyzed with the help of fitting procedures. Under certain conditions, a transition of the three-phase reaction to pure two-phase reaction occurs. To illustrate this, and for a better understanding of the phenomena, concentration profiles are presented for different degrees of the reaction and for varied simulation conditions. It is demonstrated how geometrical properties like crystal shape (cuboid with $x \neq y \neq z$) and crystal size as well as physical properties, e.g. the diffusion coefficients, govern the electrochemical behavior of mixed ionic/electronic conductors and form the basis of the current-time functions. The numerical simulation of a two-dimensional semi-infinite model of the reaction at the three-phase junction gives results comparable to an algebraical approach. The finite-difference method turned out to be suitable to solve the problems arising from the three dimensional and finite diffusion conditions and from different crystal shapes.

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**THE SOLID STATE ELECTROCHEMISTRY OF METAL
OCTACYANOMOLYBDATES, OCTACYANOTUNGSTATES, AND
HEXACYANOFERRATES EXPLAINED ON THE BASIS OF DISSOLUTION AND
REPRECIPITATION REACTIONS, THEIR LATTICE STRUCTURES AND
CRYSTALLINITIES**

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The electrochemical behavior of solid microparticles of metal (Ag^+ , Cd^{2+} , Co^{2+} , Cr^{2+} , Cu^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+}) octacyanomolybdates, octacyanotungstates, and hexacyanoferrates has been studied by voltammetry, electrochemical quartz crystal microbalance and microscopic diffuse reflectance spectroelectrochemical measurements. The solid microparticles have been immobilized on the surface of graphite electrodes prior to the electrochemical measurements. A comparative study of the cyclic oxidation and reduction of these compounds in the presence of potassium ions revealed that any interpretation of the electrochemistry requires to take into account the solubility equilibria of the reduced compounds, e.g. in case of the silver salts $\{\text{Ag}_3\text{K}[\text{X}]\}$ and $\{\text{Ag}_4[\text{X}]\}$ (with $\text{X} = \text{Fe}^{\text{II}}(\text{CN})_6^{4-}/\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$, $\text{M}^{\text{IV}}(\text{CN})_6^{4-}/\text{M}^{\text{V}}(\text{CN})_6^{3-}$ ($\text{M} = \text{Mo}, \text{W}$)). Since $\{\text{Ag}_4[\text{X}]\}$ has a lower solubility than $\{\text{Ag}_3\text{K}[\text{X}]\}$, the electrochemistry is accompanied by a conversion of solid $\{\text{Ag}_3\text{K}[\text{X}]\}$ into solid $\{\text{Ag}_4[\text{X}]\}$. Two distinct voltammetric signal systems are generated by these two compounds according to: $\{\text{Ag}_3\text{K}[\text{X}]\} \rightleftharpoons \{\text{Ag}_3[\text{X}]\} + \text{K}^+ + \text{e}^-$ and $\{\text{Ag}_4[\text{X}]\} \rightleftharpoons \{\text{Ag}_3[\text{X}]\} + \text{Ag}^+ + \text{e}^-$. When silver ions are present in the solution adjacent to the microparticles, the silver octacyanomolybdates and silver hexacyanoferrate show a chemically reversible and very stable voltammetric behavior. Despite the fact that the electrochemistry is based upon a single-electron / single-ion transfer reaction ($\{\text{Ag}_4[\text{X}]\} \rightleftharpoons \{\text{Ag}_3[\text{X}]\} + \text{Ag}^+ + \text{e}^-$) more than one electrochemical signal is observed due to the simultaneous presence of amorphous and crystalline particles. This study shows that the interplay of solubility equilibria and electrochemical equilibria is generally observed for the other metal octacyanomolybdates, octacyanotungstates and hexacyanoferrates as well.

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REACTION PATH OF PbO_2 DEPOSITION ON A PLATINUM ELECTRODE

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Lead dioxide electrodes are of great practical importance. One of the interesting fields is in sensor development. In a project concerning the development of a COD sensor use was made of a platinum electrode covered with a PbO_2 film for the production of OH-radicals.

A preliminary study of the deposition of a PbO_2 film on a platinum electrode has been done using ring-disc voltammetry. The deposition of PbO_2 occurs at potentials where also the oxygen evolution reaction occurs. By using ring-disc voltammetry it was found that during the deposition reaction less oxygen was detected at the ring electrode. This indicates that intermediates of the oxygen evolution reaction are involved in the deposition of leaddioxide. The maximum decrease of the ring current amounts to approximately 50 % compared to the ring current obtained in absence of Pb(II) . This result indicates that not OH-radicals (as was reported in literature) are implied in this reaction but another, not yet defined, intermediate must be involved in the deposition reaction of leaddioxide at the surface of a platinum disc electrode.

The result of this preliminary work is a first, coarse scheme of the mechanism of the formation of a PbO_2 layer on a platinum substrate.

**THE ELECTROCHEMICAL BEHAVIOUR OF SOLID LITHIUM COBALTATE
(LiCoO_2) AND LITHIUM MANGANATE (LiMn_2O_4) IN AN AQUEOUS
ELECTROLYTE SYSTEM**

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Lithium cobaltate (LiCoO_2) and lithium manganate (LiMn_2O_4) were synthesized by self-propagating high-temperature combustion (SPHTC) and their phase purity and composition were characterised by X-ray diffraction and inductive coupled plasma (ICP) spectroscopy. These transition metal oxides were mechanically immobilized on the surface of paraffin impregnated graphite electrodes and their cyclic voltammetric behaviour in aqueous alkali electrolytes was examined. It was shown that both the oxides undergo proton insertion upon the reduction of Co^{3+} to Co^{2+} in LiCoO_2 and Mn^{4+} to Mn^{3+} in LiMn_2O_4 while they deintercalate protons on the reverse oxidation. Scanning electron microscopy reveals spherical LiCoO_2 particles with a very narrow size distribution. Energy dispersive X-ray detection proved the absence of metal cations intercalation.

HIGH ACCURACY CONDUCTIVITY MEASUREMENTS

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The electrolytic conductivity of a solution containing ions is a measure of purity; the lower the conductivity, the purer the solution.

The measurement of this quantity is relatively simple and cheap and for water quality assessment replaces the complex measurements of the amount of different chemical species. Monitoring of water purity in such areas as pharmaceutical industry and biochemistry, power plants generating steam, semiconductor production and environmental laboratories is one of the main applications for electrolytic conductivity measurements.

Often the quality of the water directly affects the quality of other products, hence there is a growing demand for traceable conductivity measurements. To satisfy the comparability of the measurements, it is necessary to provide the user with reference solutions of long-time stability traceable to primary standards.

The present state of the art at the primary level is based on the principle of a geometrically measured, removable centre section cell. The solutions thus calibrated are then used to determine the cell constant of secondary cells and secondary conductivity solutions are calibrated using this cell.

The present method of using a removable centre section has several disadvantages. The necessity of disassembly and cleaning between measurements with and without the centre section involve the risk of contamination. For establishing traceability for pure water, the limited range of conductivities larger than 2 mS/cm is not suitable.

A new primary measurement cell allows to measure the conductivity in a wide range between 1.5 μ S/cm ... 10 mS/cm.

The two-electrode cell of well-known geometry and with variable electrode distance is made from a non porous ceramic material. Platinum is applied to the electrode bodies by a sputtering process. Due to the special construction of the cell, the distribution of the electric field within the sample is homogeneous.

STUDY OF THE CORROSION OF MOLYBDENUM, TIN(IV)OXIDE, IRON AND METAL ALLOYS IN MOLTEN ENAMEL

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All-electric melting of glass has taken an important place in glass and enamel production, because of various technical, economical and ecological advantages. In all-electric melting heat is brought into the glass melt by means of the Joule effect applying an AC current through electrodes. During this process the corrosion of the electrodes may be a disturbing factor. Currently molybdenum is predominantly used as electrode material in the glass industry. The decisive factor in the corrosion of molybdenum electrodes is the chemical composition of the melt. Since molybdenum is one of the less noble metals, it will be oxidised in the presence of nearly all other polyvalent ions in the melts.

In this study the corrosion of molybdenum (99,5% purity) and of some possible alternative electrode materials in a molten commercial enamel is investigated with the aid of electrochemical techniques. These alternative materials are iron (99,9% purity), stainless steel 304 (UNS S30400), stainless steel 316 (UNS S31600), monel 400[®] (UNS N04400), inconel 600[®] (UNS N06600) and tin(IV)oxide (98,5%, doped with CuO and Sb₂O₃). The operating temperature for all experiments was 1150°C. The polarisation resistance was deduced from the linear sweep voltammetric data and corrected for the ohmic drop between working electrode and reference electrode that was obtained with the aid of EIS (electrochemical impedance spectroscopy). Alternatively, the corrosion resistance of these materials was also determined using the weight loss method. The ranking list based on the corrosion resistance values and weight loss data is the same, except for one alloy. From the materials studied tin(IV)oxide exhibits the lowest corrosion rate in molten enamel at 1150°C.

COMPUTER SIMULATION FOR THE ELECTROCHEMILUMINESCENT ECOLOGICAL ANALYSIS (ECLA)

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For electrochemiluminescence (ECL) solutions assay (ECLA) successful ecological utilization the following should be taken into account. While many organic substances possess its own electrolysis ECL and may be defined in probe solution straightforward by so called direct ECLA (eg. carcinogenic polycyclic hydrocarbons), many others without any luminescent properties can be opened only by indirect ECLA method with appropriate ECL tag (luminol, ruthenium chelates so on). When constructing appropriate ECLA mathematical models and simulation methods for its solving one ought to consider substance in question chemical transformations on a base of continuum mechanics, chemical and electrochemical kinetics, thermodynamics etc. It is important to threat mathematically not only above mentioned two cases of ECLA, but also ECL cell (volumetric or thin-layer) configuration, electrolysis mode (pulsed or direct current/voltage). Especial attention should be paid to a possibility of conducting ECLA in flow solution by way of the flow injection analysis or high performance liquid chromatography with ECL detection. Those analysis modes can in great extent improve ECLA parameters (limit of detection, reproducibility etc.) and increase the rate of assays. That is why in our study all of those cases were considered by mathematical modelling and simulation as well as experiments were performed to prove the agreement of calculated and test results. The electrolyzed probe solutions were treated as Newtonian theology liquids either with diffusion or convective luminary mass-transfer. The latter mode is supposed to realize both in volumetric and thin-layer cells with electrolyte forced flow along plane immovable semi-infinite electrodes. The models were based on Navier-Stokes, Prandtl and Fick second law equations. Algorithms were developed for all models mathematical solving by digital simulation.

OXIDATION CHEMISTRY AND BIOCHEMISTRY OF 5-HYDROXYINDOLE

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The electrooxidation of 5-hydroxyindole has been studied in the phosphate buffers of pH range 2.1-10.1 at PGE. The initial 4e, 4H oxidation of 5-hydroxyindole leads to the formation of a dimer via quinone-imine intermediate, further oxidation of which in two 2e, 2H⁺ steps gives a tetramer. The number of electrons involved under CV condition were found as 3.8 corresponding to peak 1a and 3.9 corresponding to peak IIa. The major product of oxidation was separated by HPLC and characterized by m.p., HNMR and mass spectra as hydroxytetramer with m/z 542. The substantial changes in blood parameters after intracranial injection of a single dose of the oxidation product in albino mice at LD50 value clearly indicated that 5-hydroxyindole formed in-vivo is toxic in comparison to its oxidation product (tetramer) and hence the in-vivo conditions leading to the oxidation of 5-hydroxyindole will minimise its toxic effects.

INVESTIGATION OF CATHODIC REACTION OF SACCHARIN AND N-METHYLSACCHARIN DURING NICKEL ELECTRODEPOSITION IN ELECTROLYTES CONTAINING DIFFERENT ANIONS

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The behaviour of saccharin and N-methylsaccharin during Ni electrodeposition in electrolytes containing different quantities of sulphate, chloride and hydroxycarboxylic acids anions was investigated by determining consumption rates (V_c) of additives and accumulation rates (V_a) of cathodic reaction products. The hydroxycarboxylic acids and/or chloride anions in comparison with anions of Watt's electrolyte increase V_c of saccharin and N-methylsaccharin by acceleration of either one or both cathodic reduction reactions of carbonyl group (with and without hydrogenolysis of endocyclic C-N bond). The mixtures of the cathodic reaction products of both additives in all-chloride electrolyte differ from that of Watt's electrolyte and only the corresponding mixture of saccharin differs in the presence of hydroxycarboxylic acids at concentrations 0,04-0,10 mol·dm⁻³ used. The increase of V_a of o-toluene sulphonamide, N-methyl-o-toluene sulphonamide and N-methylbenzyl sultame shows that the adsorption of additives by a carbonyl group was increased. Decrease of V_a of corresponding benzamides makes it possible to suggest the opposite influence of investigated anions on the adsorption of additives by a sulphonyl group. The mechanism of action of additives under study is performed by their cathodic reactions. The transformation process of additives on the cathode depends on their nature, electrolytes and electrodeposits properties and on competition of all compounds and ions during adsorption on the electrode, as well as in it.

THE INFLUENCE OF FLUORIDES ON TITANIUM AND TITANIUM ALLOYS IN SIMULATED ORAL ENVIRONMENTS

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Because of its high corrosion resistance and good biocompatibility titanium and its alloys are widely used in dentistry for implants and frame-works. However, fluoride ions can attack and breakdown the protective oxide film, that is responsible for the excellent corrosion resistance properties of titanium and its alloys, leading to localized corrosion. Since fluoride ions are often introduced into the mouth, for example via hygiene products such as toothpaste and prophylactic agents, it is necessary to evaluate its potential threat to cause pitting or crevice corrosion.

A series of electrochemical test, including linear polarization resistance and potentiodynamic polarization, were conducted on commercial purity titanium, the common implant alloy Ti-6Al-4V and a beta stabilized 30%Mo titanium alloy (B21sRX) which has recently be developed for medical use. The test media chosen were based on Mulders' synthetic saliva solution (pH 4.7 to 5.0), with fluoride concentrations varying from zero to saturation.

Tafel plots and linear polarization measurements showed that the open-circuit dissolution rates of all the alloys increased with increasing fluoride levels, with the Ti-6Al-4V alloy having the lowest corrosion rate at all but the highest fluoride concentrations ($>10 \text{ g dm}^{-3}$), where the B21sRX alloy had the lowest rate.

Potentiodynamic polarization tests revealed that increased fluoride concentrations resulted in larger current densities following in the passive regime, indicating that thicker more porous oxide films were being formed

To help explain the differences observed between the various titanium alloys during the electrochemical experiments, the nature of the oxide films was further characterized by XRD and SEM. Details of these results will be discussed in the full paper.

COULOMETRIC EVALUATION OF ANTIOXIDANT CAPACITY OF BERRY, FRUIT AND VEGETABLE SAPS

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Problem of increasing storage period of natural foodstuff without loss its useful properties is very important in connection with development of food industries. Usually, autooxidation of some compounds of foodstuff is result of radical chain process with participation of peroxy radicals. Natural antioxidants prevent to this process. Substituted phenols, polyphenols, ascorbic acid, flavonoids, tocopherols and other compounds show antioxidant ability in natural products. Those compounds effectively participate in radical and ox-red reactions. Electrochemistry, chromatography and spectral analysis are used for determination of antioxidants in food products. Simple way of antioxidant capacity evaluation of foodstuff, pharmaceuticals and biological liquids was proposed in this investigation. The method is based on the use of the electrogenerated bromine compounds on platinum electrode for determination of integral antioxidant ability. The electrogenerated bromine species (Br_3^- , Br_2 , Br^* , BrO^-) react with all compounds which constitute antioxidant capacity that can be used for coulometric screening antioxidant capacity formed by compounds under investigation. The end point of coulometric titration was determined with two platinum polarized electrodes. Antioxidant capacity was expressed as a number of coulombs per 100 g of food. At these conditions data obtained characterize only water dissoluble components of berry, fruit and vegetable saps, i.e. only water-soluble forms of antioxidant could be determined. It was established that antioxidant capacity of berry decreases in order: black ashberry, snowballtreeberry, raspberry, black currant, strawberry, red currant, grape; and for vegetables: garlic, onion, cabbage, beet, egg-plant, carrot. Depending of antioxidant capacity on storage period and thermal treatment was investigated. The correlation of antioxidant capacity with being-on-the back-ability of roots and fruits or storage period was established.

VOLTAMMETRIC STUDIES ON THE CATALYTIC NICKEL PREWAVE INDUCED BY 6-MERCAPTOPURINE-9-D-RIBOSIDE (MPR)

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Catalytic nickel reduction on the dropping mercury electrode was noticed in the presence of MPR (0.002 to 0.02 mM) at pH around 7 (phosphate-acetate buffer). The signal evidenced by direct-current polarography is wave-shaped ($E_{1/2} = -0.77$ V vs. SCE) and is followed by the diffusion-controlled Ni(II) reduction wave ($E_{1/2} = -1.07$ V). The catalytic process has a kinetic character, as demonstrated by the effect of mercury column pressure and temperature. Taking into account the acid-base properties of 6-MPR as well as its complexing properties, it was proved that under the above conditions the $[\text{NiL}]^+$ complex is the main species in the solution. Accordingly, a two steps electrode reaction mechanism is proposed as follows:

1) formation of the reducible complex (the rate-determining step):



2) electron-transfer reaction, with regeneration of the free ligand:



Alternating-current polarograms and ellectrocapillary curves evidenced that the adsorption of the ligand on the mercury electrode surface is negligible and is not enhanced by the complex formation. Consequently, it was possible to determine by linear scan voltammetry the equilibrium constant ($\log \beta_{11} = 3.39$) and the rate constant ($3.19 \cdot 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$) for the step (1). This catalytic electrode process can be used for the determination of MPR by means of either stripping voltammetry or differential pulse polarography, with a detection limit of 1 or 100 nM respectively.

THE ELECTROCHEMICAL BEHAVIOUR AND ELECTROANALYSIS OF BILIRUBIN AT MERCURY ELECTRODES

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Bilirubin is a bile pigment containing in its molecule four conjugated pyrole rings.

The electrochemical behaviour of bilirubin was investigated by cyclic, linear sweep, square wave, square wave adsorption voltammetry and by direct current, fast and differential pulse polarography in aqueous and non-aqueous media. The chemical parameters of the solution and the instrumental parameters of the used techniques were examined and optimized. Linear range of bilirubin was $1 \cdot 10^{-9}$ - $5 \cdot 10^{-5}$ mol $\cdot$ L⁻¹ bilirubin and the detection limit was $5 \cdot 10^{-10}$ mol $\cdot$ L⁻¹ using square wave adsorption voltammetry (SWAdV).

ELECTROCHEMICAL BEHAVIOUR OF ERIOCHROM RED B, A N-GETEROCYCLIC AZODYE, AND ITS COMPLEXES WITH RARE EARTH

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N-geterocyclic azodyes are widely used for spectrophotometric and polarographic determination of some metals. Appearance of metal-complexes reduction peaks gives a possibility to increase sensitivity of metal determination. Therefor the electrochemical behaviour of eriochrom red B was investigated by cyclic oscillographic and alternate current voltametry with the purpose of its application for analytical determination of rare earth (RE).

Eriochrom red B (ER B) is reduced on DME in wide range of pH. At $\text{pH} < 4$ one peak (P_1) is observed, and in range of pH 4-12 two peaks (P_1 and P_2) are observed. Its potentials become negative with an increase of pH, showing that the hydrogen ion acts as a reactant in the reduction process. Change of the peaks height of ER B is coordinated with change of its exist forms. Absence of anodic peaks on the cyclic voltammograms is indication of the irreversible reduction process. Nature of reduction process is determined: the peduction of HInd form is complicated by adsorption ($\text{pK } 6.28$) and the reduction of Ind⁻ form is diffusion-controlled process with kinetic limitations. The reduction of ER B on DME gives a possibility to determine it in the water solutions with a detection limit $2.0 \cdot 10^{-7}$ (for peak P_1 at pH 10).

The electrochemical behaviour of RE-ER B complexes was studied. On adding RE to the above solution at pH 7-12, the third peak (P_3) appears with more negative reduction potential ($E = -1.0\text{V}$). The height of this peak has maximum value in the range of pH 10-11 (ammonium buffer) and it is directly proportional to the concentration of RE in the range from $8 \cdot 10^{-7}$ to $2 \cdot 10^{-5}$ M, with a detection limit equal to $6 \cdot 10^{-7}$ M. The height of P_1 and P_2 proportionally decreases with increase of RE concentration. Thus, RE can been determined by three peaks (P_1, P_2, P_3) with this reagent.

Dependence on the nature of all RE (except Pm) was studied. Sensitivity of determination is highest for heavy RE and yttrium and decreases for medium RE. This polarographic method was used to determine heavy RE in the monocrystals KMgF_3 (contents of Eu $\sim 0.5\%$) and in the compounds of the system Tb-Al.

ANTIOXIDATIVE POWER EVALUATION OF SOME PHENOLIC ANTIOXIDANTS - ELECTROANALYTICAL APPROACH

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Subsequently to the electroanalytical characterisation, it was carried out differential pulse voltammetric (DPV) studies of D- α -, D- δ - tocopherols and t-butyl hydroxitoluene (BHT) in 2,2'-diphenyl-1-picrylhydrazil (DPPH) free radical presence for providing an electrochemical approach of phenolic compounds antioxidative power estimation. It is known that a potent radical-scavenger reacts rapidly with stable free radicals [1].

Initial DPV studies performed on 6.4×10^{-8} mol L⁻¹ D- α -tocopherol (C₆H₆/C₂H₅OH 1:2, 0.12 M H₂SO₄ solvent-electrolyte system) in DPPH presence (3.4×10^{-7} mol L⁻¹) showed that the signal of α -tocopherol (0.550 V) (S_{FR}^{α}) is 2.5 times smaller than the original one, (S^{α}). For D- δ -tocopherol in DPPH presence at the concentration ratio antioxidant:free radical of 1: 5.3 (the same with α :DPPH ratio), the characteristic δ -tocopherol peak (0.780 V) it was not observed. Furthermore, for a 4.48×10^{-7} mol L⁻¹ D- δ -tocopherol concentration, a broad weak peak appears between +0.6 ÷ +0.8V vs. Ag,AgCl/Cl⁻.

The experiment performed on various ratio BHT/FR showed the maximum antioxidative effect for a 4:5 concentration (ppm) ratio. The slope of the $(\Delta i/\Delta t)_{DPPH \text{ presence}}$ is half of the slope $(\Delta i/\Delta t)$ plotted for BHT solution. It was observed, by electroanalytical way, that the antioxidative action of BHT it was partially recovered in time (about 70% of BHT initial activity).

It was provided an opportunity for electrochemical approach of antioxidative activity evaluation among the other methods which could give a correlation between particular redox properties and the antioxidative power [2].

References:

- [1] Noguchi N, Niki E, (1997) in Packer L, Cadenas E (eds.) Handbook of Synthetic Antioxidants, Marcel Dekker, New York, p. 285.
- [2] Born M., Carrupt PA, Zini R, Tillement JP, Hostettmann K, Testa B (1996) *Helv Chim Acta* 79: 1147-1158.

VIRTUAL INSTRUMENTATION FOR MULTILAYERED POROUS SILICON FORMATION

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Porous silicon (PS) obtained by anodic electrochemical etching of monocrystalline silicon (Si) in HF solution has shown efficient visible photoluminescence at room temperature [1] and has demonstrated good perspectives for optoelectronic applications [2]. Although multilayers can be easily obtained by alternating current densities, important questions have been raised concerning PS multilayer structures, such as the quality of surface roughness depending on layer formation and thickness, for instance [3]. Here we address the question of obtaining precise and reproducible multilayer structures by means of an automatically controlled apparatus with the use of virtual instrumentation.

Multilayered PS was obtained by anodization of (100)-oriented p-type substrates (400 mΩcm resistivity) by using HF (48%wt) as electrolyte. We developed a virtual instrument (VI) in LabVIEW 5.0 (National Instruments) in order to control a current source and to simultaneously measure current and voltage drop between electrodes. Moreover, acquisition, graphical presentation and storage of experimental data are performed on line within the system, composed by a personal computer, GPIB board and low-cost laboratory equipment.

Through the designed graphical user interface one can choose current densities, intervals for each density and number of periods for current steps. Control of other process variables such as various waveform generation are being implemented. In this work PS multilayers were formed applying 10mA/cm² for 5min, 100mA/cm² for 2min and 10mA/cm² for 5min, subsequently. The VI automatically controls and switches current density for the predefined periods of time.

The obtained PS multilayers have been measured and characterized by Raman spectroscopy and scanning electron microscopy. Main variables analysed were porosity, layer formation, reproducibility and precision in layer formation depending on time and current density.

References

- [1] Canham, L.T. "Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers". *Applied Physics Letters*, v.57, p.1046-1048, 1990.
- [2] Loni, A; Canham, L.T., Berger, M.G.; Arens-Fischer, R.; Munder, H., Luth, H.; Arrand, H.F.; Benson, T.M. "Porous silicon multilayer optical waveguides". *Thin Solid Films*, v. 276, p. 143-146, 1996.
- [3] Setzu, S., Ferrand, P., Romestain, R. "Optical properties of multilayered porous silicon", *Materials Science and Engineering*, v. B69-70, p. 34-42, 2000.

CATALYTIC WAVES OF HYDROGEN IN VOLTAMMETRIC CONTROL OF IMMUNOREACTIONS

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Immunoassay techniques based on electrochemical determination of non-enzymatic labels seems to be a promising approach for the development of alternative immunoassay methods. These techniques normally require a single stage analysis based on a highly sensitive determination of a non-enzymatic label. The use of electrocatalytic processes in this case allows to increase assay sensitivity and to simplify assay procedures. The attempt to use of catalytic waves of hydrogen as analytical signal was undertaken. For this purpose antibody (Ab) and antigen (Ag) of ribonuclease (RNA) were used as immunoreagents. Co(II) and Ni (II) ions was used as labels. Previously was established that metal ions not adsorbed on the surface of nitrocellulose membrane both in presence and in absence of coupling agents such as diethylentriaminopentaacetic acid and ethylendiaminetetraacetic acid and also in presence of immobilized Ab against RNA. It was experimentally established that maximum catalytic effect observed at the Co(II) concentration 1×10^{-4} M and Ag RNA concentration 1.6×10^{-9} M. The linear dependence of peak current of Co(II) at $E = -1.4$ V on Ag concentration was observed in the concentration range $1.6 \times 10^{-9} - 8.1 \times 10^{-11}$ M and in pH range 7.2-10.0. This assay consists of four steps:

1. Formation of immunocomplex Ab-Ag in the tris-HCl buffer solution with pH 7.0 on the surface of nitrocellulose membrane with immobilized Ab during 30 min
2. Remove uncoupled Ag
3. Destruction of immunocomplex in glycine-HCl buffer solution with pH 2.5 during 1 min
4. Neutralization of aliquot by 2 M ammonium
5. Electrochemical detection of analytical signal in ammonium buffer solution with pH 9.5

The detection limit was 1.6×10^{-11} M for Ag RNA with standard deviation not more than 0.15. In such a case the possibilities of electrocatalytic reactions (high sensitivity with respect to determining compounds and ability for selective interaction with definite substances) are fully realized.

APPLICATION OF AN ELECTROMETRICAL APPROACH TO MONITOR FORMATION OF SPECIFIC IMMUNE COMPLEXES ON THE POROUS SILICON AND METAL SURFACES

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The current work is devoted to the use of an electrometrical method, which is capable of providing very sensitive registration of the changes of physical-chemical properties of the test structures, for the development of a direct technique to monitor interaction between biomolecules. The influences of some biological molecules and their specific complexes on the I-V characteristics of the surface-barrier structures (SBS) with the layer of ultra-thin metal or porous silicon (PS) were studied.

The experimental metal-semiconductor specimens were prepared by vacuum beam-evaporation of nickel on the surface of silicon. The samples of the SBS with a thin layer of PS were obtained according to the standard technology, in which monocrystalline silicon wafers of p-type and electrolytes on the basis of hydro-fluoric acid were used. The thickness of the PS films was 100, 150, 200, 250, 300 Å. Human myoglobin (Mb) and specific mouse monoclonal antibodies to Mb were used as examples of biological molecules. In order to study electrical characteristics of the thin metal layer or PS their surfaces were with: separate proteins; mixture of Mb and its specific antibodies; Mb and consequent deposition of its specific antibodies.

The obtained results suggest that I-V characteristics of both SBS with the layer of ultra-thin metal and PS undergo changes after the deposition of proteins on their surfaces. Moreover, the deposition of the mixture of Mb with its specific antibodies caused the most essential changes in the I-V characteristics in comparison with the I-V parameters after the placement of Mb and its specific monoclonal antibodies separately or successively. It was shown that the optimum thickness of the thin metal or PS layer necessary for the development of a maximum response is equal to 200 - 300 Å.

On the basis of obtained results the electrometrical method seems to be suitable for the direct and express determination of formed specific immune complexes.

INFLUENCE OF STRUCTURAL STRESSES ONTO KINETICS OF ALUMINIUM ANODIC OXIDATION

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The anodic oxidation process is one of the most frequent protection method of aluminium and its alloys. The knowledge of the aluminium electrochemical oxidation mechanisms enables to estimate the optimum conditions of the anodization procedure, as well as gives deep insight into the aluminium passivation process itself.

This work is concerned with the investigation of anodic oxide film properties, produced as a result of aluminium sample anodization specified by variations thicknesses in the 4 % aqueous oxalic acid solution in galvanostatic conditions. The obtained results evidence that under anodization in the same conditions the thicker oxide layers are formed on the wafers with higher initial thickness.

It is assumed that the various thickness of aluminium oxide films is due to the various electric intensity. It is shown that this fact is attributed to the emergence of non-identical structural stresses in the samples with aluminium various initial thicknesses during anodization process.

Based on the proposed insight into the aluminium internal stress effect on the kinetics of the anodic oxide film growth the anodic oxidation mechanism model is suggested. It is derived a formula for aluminium oxide layer thickness being formed plotted against aluminium initial substrate thickness and anodization time. The obtained theoretical dependencies of aluminium average anodization rate on aluminium initial substrate thicknesses are well agreed with the experimental results.

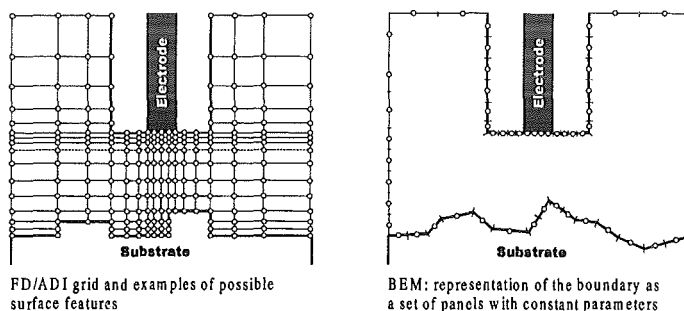
APPLICATIONS OF THE BOUNDARY ELEMENT METHOD FOR NUMERICAL SIMULATIONS IN SECM INVESTIGATIONS

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Scanning electrochemical microscopy (SECM) is an established scanning probe technique that is sensitive to surface reactivities. The local probe is an amperometric ultramicroelectrode (UME). However, the UME current depends not only on the surface reactivity but also on topographic features of the sample and the UME geometry.

To extract quantitative data from the SECM measurements, digital simulations should be carried out, which compute the UME current for a given sample and probe geometry, including sample-probe distance. Most SECM problems have been modeled by the finite difference (FD) or alternate-direction implicit methods (ADI).¹⁻² Implementation of these methods in case of non-axisymmetric leads to huge difficulties in finding a suitable coordinate transformation and enormous computation times. Recently a series of publications by Fulian et al.³⁻⁵ suggested the boundary element method (BEM)⁶ as a method that would allow to compute steady state UME currents for just these practically important situations. The BEM replaces the differential equations defined in the volume by an integral equation defined on the boundary of the simulation space, thus reducing the dimensionality of the computation problem. Further advantages for SECM simulations include the ease, with which complicated UME and sample



geometries can be considered.

As an example, first results for sample-probe approach curves are presented for different UME geometries. Requirements to achieve accurate results are discussed.

- ¹ A.J. Bard, M.V. Mirkin, P.R. Urwin, D.O. Wipf *J. Phys. Chem.* **1992**, *96*, 1861 – 1868
- ² J. L. Amphlett, G. Denault *J. Phys. Chem. B* **1998**, *102*, 9946 – 9951
- ³ Q. Fulian, A.C. Fisher *J. Phys. Chem. B* **1998**, *102*, 9647 – 9652
- ⁴ Q. Fulian, A.C. Fisher, G. Denault *J. Phys. Chem. B* **1999**, *103*, 4387 – 4392
- ⁵ Q. Fulian, A.C. Fisher, G. Denault *J. Phys. Chem. B* **1999**, *103*, 4393 – 4398
- ⁶ Brebbia, C.A.; Dominguez, J. *Boundary Elements: An introductory course*, Computational Mechanics Publications; Southampton and Elsevier, UK, **1994**

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van Bennekom, W.P.	see Hoogvliet, J.C.	C 08, E 10
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Visco, G.	see Sammartino, M.P.	C 28
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Vogel, I.	see Baltruschat, H.	C 02
Vogt, H.	see Köster, O.	B 03
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