
POSTERS

PP-01**ELECTROCHEMICAL STUDY OF 3-(AZIDOMETHYLENE)DIHYDROFURAN-2-ONE****VOJTĚCH ADAM^a, RENÉ KIZEK^a, CTIBOR MAZAL^b, LIBUŠE TRNKOVÁ^{b*}**

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Organic azides are important compounds not only in organic synthesis but also in medicine as based molecule for preparation of drugs for HIV positive patients (*e. g.* azidothymidin)¹. From electrochemical point of view azide group is subject to reduction. In this study we discussed the reduction of 3-(azidomethylene) dihydrofurane-2-one (AZMDF), which occurs in two conformations: (*E*) form and (*Z*) form. These furanoid azides were prepared due to studying of reactivity of α -tosyloxymethylenlactones². Using linear sweep or cyclic voltammetry and elimination voltammetry with linear scan (EVLS) (ref.^{3–5}) in connection with a mercury electrode, signals of (*E*) and (*Z*) forms of AZMDF were clearly distinguished. In addition, we optimized experimental conditions to enhance sensitivity of determination of target molecules. The highest reduction signals of both isomers were measured in KCl, but the best distinguishing of both isomers was determined in the presence of borate buffer. While (*E*) form has the highest reduction peak at pH 7.94, (*Z*) form at pH 8.84. The detection limit was evaluated down to 1 mM. It was found by EVLS that the reduction process of azide group is diffusion-controlled process and this process is little dependent on pH.

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PP-02**SIMULTANEOUS DETERMINATION OF ZINC (II), LEAD (II) AND COPPER (II) AT BISMUTH FILM ELECTRODE BY MULTIVARIATE CALIBRATION****GEORGINA M. S. ALVES, JÚLIA M. C. S. MAGALHÃES, HELENA M. V. M. SOARES***

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In 2000, a new type of electrode, the bismuth film electrode (BiFE) was proposed as an environmental friendly alternative to mercury film electrode (MFE) for anodic stripping voltammetry (ASV) measurements of heavy metals¹. Most metals, with exception of copper, form binary alloys with bismuth, and hence, display well defined and undistorted peaks which permit convenient multi-elemental measurements². However, simultaneous determination of Cu (II), Pb (II) and Zn (II) ions using BiFE electrodes is prone to interferences, which can be attributed to the formation of intermetallic compounds (*e.g.* Cu-Zn) and poor resolution between adjacent peaks of Cu (II) and Bi (II), ref.^{2–4}. The chemometric tools are useful to solve this kind of drawbacks⁵ and thus the use of these tools deserves further research.

This communication reports the simultaneous determination of Pb (II), Zn (II) and Cu (II) ions at low concentration levels (ppb) by square wave anodic stripping voltammetry on a BiFE plated *in situ* at a glassy carbon electrode (GC). Discrete wavelet transform was applied for processing copper and bismuth overlapped peaks, improving the detection limit for Cu (II) ions down to 2 ppb. The construction of multivariate calibration models, based on partial least squares regression (PLS), allowed the simultaneous determination of Pb (II) (in the concentration range 2.5 to 70 ppb), Zn (II) (10 to 120 ppb) and Cu (II) (2 to 15 ppb) ions with prediction errors below 10 %.

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PP-03
ELECTROCHEMICAL BEHAVIOR OF DNA AND RNA HEPTAMERS AT A MERCURY ELECTRODE

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Hairpins play an important role in many biological processes including triplet repeat expansion associated with neurodegenerative diseases (fragile X syndrome, Huntington's disease, Friedreich's ataxia or myoclonic epilepsy)¹. The shortest and the most stable hairpin is formed by the DNA heptamer d(GCGAAGC) (ref.^{2,3}). This sequence can be found in replication origins of phage ϕ X 174 and herpes simplex virus, in a promoter region of an *Escherichia coli* heat-shock gene and in rRNA genes. In this study, we studied d(GCGAAGC) hairpin and its RNA analog by means of adsorptive stripping voltammetry. Both DNA and RNA heptamers, adsorbed on mercury electrodes, provided voltammetric reduction signals of adenine and cytosine (A and C) and oxidation signals of guanine (G). The dependences of these voltammetric signals on pH, accumulation time, scan rate and loop sequences were determined. For the resolution of A and C reduction signals and for the evaluation of nature of anodic processes of G signal in both heptamers elimination voltammetry with linear scan (EVLS) was utilized⁴⁻⁶.

Our results show that EVLS, as a fast, simple, and inexpensive electroanalytical tool, is effective not only for the detection and resolution of A and C bases in oligonucleotides and for the characterization of nature of electrode processes, but also for the sensitive detection of changes in primary and secondary structure of nucleic acids' fragments.

This work was supported by INCHEMBIOL (MSM 0021622412), BIO-ANAL-MED (LC06035) from the Ministry of Education, Youth and Sports of the Czech Republic

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PP-04
VOLTAMMETRIC DETERMINATION OF B₁, B₂ AND C VITAMINS IN PHARMACEUTICAL PRODUCTS

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Vitamins are organic compounds which are required for the normal growth and maintenance of life of animals, including man, who, as a rule are unable to synthesize these compounds by anabolic processes¹. Most of the vitamins induce reasonable polarographic and voltammetric responses and can be qualitatively as well as quantitatively determined voltammetrically²⁻⁴, without interference resulting from the presence of each of them and other compounds under optimum experimental conditions.

In the work, the cyclic renewable mercury film silver based electrode (Hg(Ag)FE) (ref.⁵) was proposed as a working electrode for B₁, B₂ and C vitamins detection in pharmaceutical products. The Hg(Ag)FE, refreshed before each measurement, demonstrates many properties specific only for the hanging mercury electrode. The preparation of the Hg(Ag)FE electrode is very simple and economically acceptable, it has a very good stability, and the renovation of the surface is easy. The Hg(Ag)FE is characterized by very good surface reproducibility ($\leq 2\%$) and long-term stability (more than 2 thousand measurement cycles).

Before the measurements realized by staircase, normal pulse and differential pulse voltammetry methods, optimization of the supporting electrolyte composition, preconcentration conditions and other important parameters was done.

The influence of organic interfering substances was done by addition of Tritonu X-100: 5 mg L⁻¹ in the case of B₁ vitamin and 60 mg L⁻¹ in the case of B₂ vitamin. In the presence of Tritonu X-100 stability of the electrode parameters and repeatability of the signal were tested. Also procedure of Hg(Ag)FE electrochemical conditioning was proposed.

The developed methods were successfully applied and validated by studying the standard substances and various commercially available pharmaceutical products.

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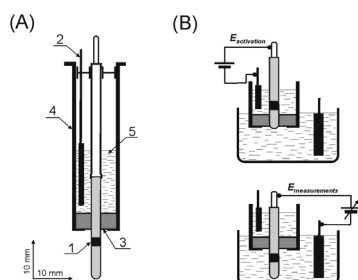
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PP-05
THE RENOVATED GOLD RING ELECTRODE

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In this preliminary note, a new type of “mercury-free” working electrode – the renovated gold ring electrode (RGRE) – is presented. The only four constituents of the RGRE: a specially constructed gold ring electrode (1), a silver sheet used as silver counter/quasi-reference electrode (2) and a silicon O-ring (3) are fastened together in a polypropylene body (4). The renovation of this electrode is carried out through mechanical removal of solid contaminants and bubbles of the gas (hydrogen) and electrochemical activation in the electrolyte (5) which fills the RGRE body^{1,2}. The most important advantages of this construction are: possibility of transfer of the electrode from the activation cell to the measurement cell without any contact with air in the conditions of the minimal distortion of the compact part of the double layer. Excellent repeatability and reproducibility – also in organic samples solutions – were reached in a period of a few weeks, through the renovation of the electrode surface before each measurement.



As it was shown on selected examples, the RGRE exhibits good performance in underpotential deposition stripping voltammetry (UPD-SV) (ref.³) applied for the determination of Pb(II) and Cu(II) traces⁴ in synthetic solutions with and without surfactants and in certified reference materials. The obtained results confirm that the RGRE may be in the future incorporated into out-of-laboratory sensor systems.

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PP-06
POLAROGRAPHIC STUDY OF THE INTERACTION BETWEEN CUCURBIT[6]URIL AND DIVALENT CATIONS

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The cucurbit[n]uril family (CB[n], $n = 5-10$) is a group of macrocyclic, pumpkin-shaped compounds comprising n glycoluril units enlaced by methylene groups. They have common properties as two polar “portals” (due to ureido carbonyl groups), a hydrophobic interior, and a modest or low solubility in water that is enhanced if an alkaline or alkaline-earth cation is present. The main difference among them is the diameter, which depends on the number of glycoluril units; they have different recognition properties due to this feature. Although much of the work with CB[n] has been done in supramolecular chemistry with organic compounds¹, there are also researches on their interactions with metals. Some of them deal with the interaction to assemble supramolecular adducts in solid state². Buschmann’s group reported the stability constants of several metal complex with CB[5], a homologous of CB[5], and CB[6], either alkaline and alkaline-earth³ or heavy metals⁴.

This work was done using a static drop mercury electrode. In our knowledge, no group has surprisingly studied the interaction between any CB[n] and metal using this electrode. The employed macrocyclic ligand was CB[6], previously dissolved. This study was done with zinc (II), cadmium (II), manganese (II), cobalt (II) and nickel (II) in different supporting electrolytes. We found that the stoichiometry depends on the metal. Their stoichiometry varied from 2:1 to 4:1 (metal:CB[6]). In some cases the complex was electroactive and thus the stability constant can be calculated.

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PP-07**HIGH-STABLE PLANAR SENSORS FOR HYDROGEN PEROXIDE DETECTION BASED ON PRUSSIAN BLUE STABILIZED WITH NICKEL CYANOFERRATE****ANASTASIYA V. BORISOVA, NATALYA A. SITNIKOVA, ARKADY A. KARYAKIN**

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Hydrogen peroxide is considered as an important analyte nowadays. It is known as a chemical threat agent and the most valuable marker for oxidative stress¹.

We already reported on Prussian Blue as the most advantageous hydrogen peroxide transducer². The main disadvantage of the Prussian Blue based sensing layers is their inherent instability.

The approach for stabilization of Prussian Blue films with nickel and cobalt cyanoferrates has been already proposed in our laboratory³. However, this method involves electrochemical stage which is non-applicable for mass production of sensors.

In this work we proposed a novel method for Prussian Blue films stabilization with nickel cyanoferrate. This procedure is based on open-circuit deposition of Prussian Blue and nickel cyanoferrate by analogy with interfacial polymerization⁴.

We used screen-printed electrodes (Rusens Ltd.) to simplify the procedure of sensor production and to lower their cost.

The novel method of stabilization Prussian Blue films allows to exclude electrochemical stage and to simplify the procedure of electrodes modification. Analytical characteristics of developed sensors are tested in FIA. The linear calibration range is prolonged over four orders of magnitude of hydrogen peroxide concentrations from 1×10^{-7} to 1×10^{-3} M. The developed sensors display dramatically improved operational stability at continuous monitoring of hydrogen peroxide. Under the constant flow of hydrogen peroxide (1 mM) sensors hold 100 % activity during almost half an hour with subsequent very slow decay.

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PP-08**DETERMINATION OF TRACE ANTIMONY BY ADSORPTIVE STRIPPING VOLTAMMETRY USING CYLINDRICAL MERCURY FILM ELECTRODE****ANNA BUGAJNA, ROBERT PIECH*, WLADYSLAW W. KUBIAK, BEATA PACZOSA-BATOR**

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Antimony and his chemical compounds are very ecotoxic¹. This element is found in two oxidation states Sb(III) and Sb(V) in environmental, biological and geochemical samples². The toxicological behavior of antimony depends than his oxidation state. Antimony compounds in the oxidation state +3 are more poisonous than those in the oxidation state +5 (ref.³).

A variety of voltammetric methods has been proposed for Sb and compounds, including anodic stripping voltammetry (ASV) (ref.⁴) and adsorptive cathodic stripping voltammetry (AdSV) at a hanging mercury drop electrode⁵.

In the work a sensitive and selective adsorptive stripping voltammetry for the determination of trace antimony using cylindrical mercury film silver based electrode is presented.

The proposed procedure electrochemical determination of antimony under optimized conditions allows obtain the detection limit as low as 0.17 nM (21 ng L^{-1}) for preconcentration time of 90 s. The method was successfully applied for antimony determination in environmental samples.

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PP-09**STRIPPING VOLTAMMETRIC DETERMINATION OF As(III) IN NATURAL WATER SAMPLES WITH COMPLICATED MATRIX****MALGORZATA GRABARCZYK, MIECZYSLAW KOROLCZUK, KATARZYNA TYSZCZUK**

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Knowledge of the speciation of arsenic in natural water is important because the bioavailability and the physiological and toxicological effects of arsenic depend on its chemical form. Because inorganic compounds of arsenic are more toxic than the organic ones and toxicity of As(III) is higher than that of their pentavalent species procedures of determination of this form are necessary. A number of voltammetric methods for As(III) determination with low detection limit have been recently developed, but only some of them can be used for As(III) determination in the presence of the organic substances commonly present in natural samples such as humic substances and surface active compounds. It is related to the fact that even small concentrations of organic matter often cause a decrease or decay of the arsenic voltammetric signal.

This communication provides a simple and fast procedure for As(III) determination which allows for the analysis of natural samples with complicated matrix containing high concentration of surfactants and humic substances. The proposed procedure is based on the stripping voltammetric method of As(III) determination in the presence of copper and HCl as supporting electrolyte. All experiments were carried out with an μ Autolab analyzer and a controlled growth static mercury electrode in the HMDE mode. A three-electrode voltammetric classic cell consisting of an Hg working electrode, a Pt auxiliary electrode and an Ag/AgCl reference electrode.

The interference from matrix of natural samples was drastically decreased by adding Amberlite XAD-7 resin to the sample. The resin is added directly to the voltammetric cell to the analysed sample before the deaeration step and interferences such organic substances are removed from the sample during the deoxygenation step. Therefore the proposed voltammetric procedure is very simple and fast. To obtain the optimal conditions of removing organic matter by adsorption on Amberlite XAD-7 resin composition and concentrations of the supporting electrolyte, the amount of the resin and the time of sample contact with resin were studied. The experiments were performed for synthetic samples containing surface active compounds such as Triton X-100, SDS and CTAB (nonionic, anionic and cationic surfactant, respectively) and humic substances such as humic and fulvic acids. The presented method was successfully applied to the speciation of arsenic in natural water samples and certified reference material. The attractive parameters and the successful application of the elaborated procedure holds great promise for exploiting it for environmental and industrial monitoring of As(III).

PP-10**ELECTROCHEMICAL DEPOSITION – STRIPPING ANALYSIS BY ONLINE ELECTROCHEMICAL FLOW CELL – MASS SPECTROMETRY****VITALY GUTKIN, JENNY GUN, OVADIA LEV**

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During the last years the Laboratory of Environmental Chemistry is developing a powerful tool for analysis of the intermediates and by-products of electrochemical reactions by electrochemical flow cell coupled directly to an on-line mass spectrometer¹⁻⁴. On-line methods are always preferable in electrochemistry over preparative electrolysis followed by *ex situ* analysis, since they minimize interferences, contaminations, electrode fouling and oxygen penetration. We have introduced a thin radial flow cell equipped with a miniature working electrode. The miniature electrode guarantees minimal uncompensated Ohmic drop within the flow cell, and the very thin layer configuration provides high conversion even for small electrodes at relatively high flow rates.

Recently, we have developed a modified version of the EC/ESI-MS instrument for electrochemical preconcentration, desorption and analysis of analytes by EC/ESI-MS (ref.⁵).

A methodology for on-line preconcentration of analytes and their subsequent electrochemically induced delivery to an on-line electrospray mass spectrometer is introduced. The approach is based on electrodeposition of an active metallic layer, silver deposit in this particular case, subsequent specific accumulation of the target analyte by electrochemical or chemical means onto the active layer, and finally oxidative electrostripping of the conductive layer along with the supported analyte to an on-line mass spectrometer. We demonstrate the new concept by selective electrochemical deposition of homocysteine and other organothiols directly on the working electrode of a miniature flow cell. The same approach was extended to the conjugation of the target analyte (avidin as a test case) to a thiolated ligand (biotin in this case) that was electrodeposited on the silver coated surface. Electrostripping of the silver dissolves the target species and allows their delivery to an on-line ESI-MS.

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PP-11
SIMULTANEOUS DETERMINATION OF PHENOLIC
AND AMINIC ANTIOXIDANTS IN LUBRICANT OILS

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This paper deals with the voltammetric determination of synthetic phenolic and aminic antioxidants in lubricant oils applying linear sweep voltammetry. Antioxidants belong to the additives, which prevent the attrition of oils and prolong its lifetime^{1,2}. The measurements were carried out using gold working electrode, Ag/AgCl/KCl as reference and platinum wire as an auxiliary electrode in acid medium of sulphuric acid with addition of acetonitrile.

The phenolic antioxidants present in the sample in absence of aminic ones, can be determined directly after their extraction by ethanol. The measurements in mixture of both types of antioxidants in oils are complicated by the fact that the present aminic antioxidants influence the determination of phenolic ones. The results are lower. For the elimination of mentioned interference new method, based on known reaction of aromatic amines with nitric acid to nitrosamine, was evaluated and optimized.

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PP-12
NEW MULTIPURPOSE ELECTROCHEMICAL
ANALYZER FOR SCIENTIFIC AND ROUTINE TASKS

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The presented device is a new modernized and improved construction of the analyzer which different versions were developed in our team for past 30 years. In this construction the modern fully integrated chips were applied, dedicated for measurements of low level of the recorded value.

The proposed multipurpose analyzer ensures complete measuring features and may control different electrochemical sensors, such as: different types of mercury film electrodes (Hg(Me)FE) (ref.¹), renewable solid electrodes², microelectrodes, corrosion cells, which are fully integrated with the device. Among other, it is the only instrument which fully

supports the Controlled Growth Mercury Dropping Electrode (CGMDE) (ref.³). The techniques accessible in the analyzer are: staircase, normal pulse, differential pulse, square-wave, linear sweep voltammetry, stripping voltammetry, chronoamperometry, etc. Numerous measuring parameters in each method may be flexibly chosen, what gives practically unlimited possibilities of the experiment programming. The recorded curve is visualized, stored and may be separately, or as a part of the set of curves, transformed and interpreted in unlimited manner. Different typical and more advanced signal processing procedures are built-in and easy accessible⁴⁻⁷. For example, smoothing and baseline correction may be done using various algorithms. Also the procedure which enables quantitative determinations is available – calibration may be done using different strategies.

There are almost unlimited possibilities of application of the analyzer. These are scientific investigations of electrode processes, testing of modern sensors, determination of non-ionic surface-active substances and typical routine analysis of artificial, environmental, pharmaceutical samples. Also corrosion processes may be investigated using this system.

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PP-13
RENEWABLE SOLID ELECTRODES –
APPLICATIONS IN THE PRESENCE OF DOUBLE
LAYER MODIFICATORS

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In stripping voltammetry^{1,2} which is widely used in electroanalysis, a hanging mercury electrodes (HMDEs) is usually applied. A characteristic feature of the HMDEs is high rate of adsorption of various surface-active species (SAS) on the mercury surface. This property can be used in analysis of surfactants³ but also makes it impossible to realize the analy-

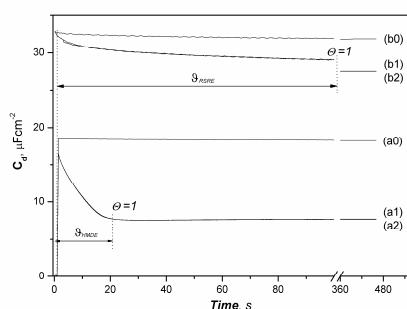


Fig. 1. C_d - t for HMDE (a0) and RSE (b0) in 10 mM (HNO_3 + KCl); Curves: (a1) and (b1) after 5 mg L^{-1} Triton X-100 addition, (a2) and (b2) after generation of the new mercury drop (HMDE) and renovation of RSE

sis of non-pretreated samples. This problem does not concern renewable solid electrodes (RSE) because the adsorption time (ν) of SAS on solid electrodes is much longer than in the case of the HMDE, while the effectiveness of renovation is comparable (Fig. 1, ref.⁴).

The proposed approach was verified by the quantitative determination of Pb and Cd ions in CRM water samples, spiked with SAS on a renovated Ag, Au, Ti(C, N) electrodes. It was concluded, that Pb and Cd peaks on the RSE were unaffected by polyethylene glycols in the tested concentration range 0 – 200 mg L^{-1} . Also SDS and Triton X-100 in concentrations up to 100 mg L^{-1} had marginal influence for the peaks height of both metals. Moreover, in this work the new automatic algorithms of signal processing and quantitative analysis were developed.

The study was supported by the Ministry of Science and Education (AGH Project No. 11.11.160.799).

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PP-14

VOLTAMMETRIC DETERMINATION OF SUCCINYLACETONE BY ESTERIFICATION

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Succinylacetone (SA, 4, 6-diketoheptanoic acid) is primary diagnostic metabolite for inherited disorder hepatorenal tyrosinemia type I (ref.¹). Tyrosinemia, type I is a devastating

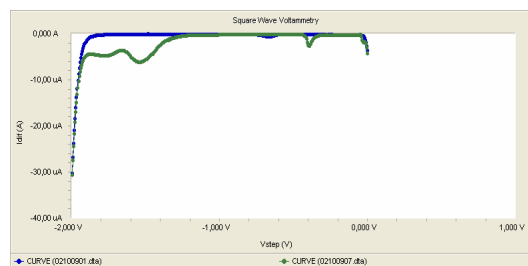


Fig. 1. The voltammogram of the standard solution of SA after reacted with methyl alcohol in the presence of 0.05 M phosphoric acid (pH 2)

disorder of childhood that causes liver failure, painful neurologic crises, rickets and hepatocarcinoma². In this work a voltammetric determination of SA in amniotic fluid was investigated for assisting the early diagnosis of tyrosinemia type I.

All voltammetric measurements were carried out with a Gamry electrochemical analyzer. A hanging mercury drop electrode (HMDE) was used as a working electrode. Potassium chloride (0.1 M) was selected as supporting electrolyte. The square wave voltammetric operating conditions were as follows: equilibration period: 5 s, voltage step: 0.01 V, pulse amplitude: 0,1 V, frequency: 100 Hz.

Under operating conditions, succinylacetone gave an irreversible reduction peak at $-1.68 \text{ V vs. Ag/AgCl}$ reference electrode. The electrochemical reduction of SA was calculated to proceed with one electron transfer. Linearity range of calibration curve was between 1.23 – $4.41 \times 10^{-4} \text{ M}$. Limit of detection (LOD) and limit of quantification were calculated as $2.92 \times 10^{-5} \text{ M}$ and $9.76 \times 10^{-5} \text{ M}$ respectively. This LOD value is inadequate for the determination of succinylacetone in biological fluids. Esterification of succinylacetone with methanol in acidic medium amplified the electroreduction current while producing two peaks as shown Fig. 1. Esterification procedure was useful not only for improved the LOD but also for the extraction of succinylacetone from amniotic fluid.

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PP-15
IMPROVEMENT OF ENZYME
BIOELECTROCATALYSIS USING SUBSTRATE
CONTAINING ELECTROACTIVE POLYMERS

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Bioelectrocatalysis is the acceleration of electrochemical reactions by biological catalyst¹.

We show the improvement of bioelectrocatalysis using electroactive polymers containing analogues of the enzyme substrates in cases of different enzymes: hydrogenases and cellobiose dehydrogenases from different sources.

The latter having affinity to enzyme active site or its electron-transport chain are expected to provide proper orientation of these biological catalysts. Moreover, the use of highly electroactive artificial substrates is expected to improve electron exchange between the enzyme electron transport chain and the electrode.

Indeed, hydrogenase from *T. roseopersicina* being immobilized over polypyrrole containing viologen groups as substituents displays in average five times improved electrocatalytic activity as compared to the enzyme immobilized directly on carbon surface.

The dramatic effect of using promoters was observed in case of hydrogenase from *D. baculatum*. Where as directly on carbon no bioelectrocatalysis can be observed, immobilization of this enzyme over polypyrrole-viologen resulted in the most active hydrogen enzyme electrode².

Cellobiose dehydrogenase from *Myriococcum thermophilum* being immobilized onto carbon screen printed electrodes displays the direct bioelectrocatalysis. Electropolymerized Methylene Green and in particular electropolymerized Methylene Blue promotes dehydrogenase bioelectrocatalysis very efficiently.

We believe that the reported conception will help to involve much more enzymes in efficient bioelectrocatalysis. This would led to elaboration of novel biosensors, enzyme fuel electrodes for biofuel cells and even allow to develop useful systems for specific electrosynthesis.

Financial support through RFFI 09-03-01126-a and contract 959 from RF Ministry of Education are greatly acknowledged.

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PP-16
ELECTROPOLYMERIZATION OF N-SUBSTITUTED
PYRROLES FOR DEVELOPMENT OF LACTATE AND
GLUCOSE BIOSENSORS BASED ON PRUSSIAN
BLUE MODIFIED ELECTRODES.

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Entrapment in electropolymerized films remains the most popular electrochemical approach for biosensor fabrication. Effective and inexpensive biosensors for lactate and glucose received by electropolymerization would find wide application in clinical diagnostics, sports medicine, food and agricultural raw materials quality control as well as the control of fermentation processes.

Screen-printed electrodes (Rusens Ltd., Russia) have been used to simplify the procedure of sensor production and to decrease their cost. The working surface of planar electrodes have been modified by Prussian Blue which is known to be the most effective hydrogen peroxide transducer¹. Lactate oxidase and glucose oxidase were immobilized into conducting polymer films on the surface of planar electrodes modified with Prussian Blue. Different *N*-substituted pyrrole monomers synthesized by professor S. Cosnier (Grenoble University) were electropolymerized to obtain the conducting polymer². The analytical characteristics of the resulted lactate biosensor in FIA were: the sensitivity of $190 \pm 14 \text{ mA M}^{-1} \text{ cm}^{-2}$, linear dynamic range of $5 \times 10^{-7} - 5 \times 10^{-4} \text{ M}$, response time about 30 seconds, high operational stability (more than 100 measurements in FIA). Glucose biosensor has the following characteristics: the sensitivity of $44 \pm 4 \text{ mA M}^{-1} \text{ cm}^{-2}$, linear dynamic range from 5×10^{-6} to $5 \times 10^{-3} \text{ M}$ and high operational stability. The application of lactate and glucose biosensors for food quality control (kvass, milk products) has been shown³.

Highly stable and suitable for multiple use biosensors with a low detection limit may be applied also for the noninvasive lactate and glucose analysis in clinical diagnostics.

The authors are grateful to professor S. Cosnier (Grenoble University, France) for providing samples of N-substituted pyrroles. Financial support by the RFBR grant 06-03-33013-a, INTAS innovation grant 05-10000070429, Contracts of Federal Agency for Science and Innovation №02.512.12.2028 №02.512.11.2326 are greatly acknowledged.

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PP-17**STRIPPING VOLTAMMETRIC DETERMINATION OF METHYLMERCURY IN THE PRESENCE OF INORGANIC MERCURY****MIECZYSLAW KOROLCZUK, ANNA STEPNIOWSKA, KATARZYNA TYSZCZUK**

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Mercury has been widely recognized as one of the most hazardous of environmental pollutants and a highly dangerous element due to its accumulative and persistent character in the environment and biota. Although inorganic mercury is highly toxic, methylated forms of mercury are even more dangerous since they can be concentrated through the food chain as a consequence of their high solubility in lipids. Methylmercury is the most commonly occurring methylated form of mercury. For these reasons analytical tools for determination of methylmercury at low concentration levels are necessary.

Electrochemical methods require relatively cheap instrumentation, offer low detection limits and often allow for direct determination of the species of interest. Most of the voltammetric procedures for quantification of methylmercury are based on methylmercury reduction to its radical and then its fast reoxidation. Recently a new way of elimination of Hg(II) on stripping voltammetric determination of methylmercury was proposed. Its relay on complexation of Hg(II) by DTPA (ref.¹).

In this communication a new procedure for methylmercury determination was described. In this procedure to increase the selectivity of methylmercury determination a gold film electrode coated with Nafion and complexation of Hg(II) by DTPA we exploited. To obtain low detection limit for methylmercury optimization of experimental parameters of electrode preparation and deposition of methylmercury was performed. Gold film electrode was prepared by electrodeposition of gold on glassy carbon from solution containing 6×10^{-4} M AuCl₃ + 0.025 M HCl + 4 g L⁻¹ urea. The gold film electrode was then covered by Nafion film using pneumatic nebulizer from AAS apparatus. For this purpose 0.5% solution of Nafion in buthyl alcohol was used. The electrochemical procedure of electrode regeneration after the measurement was proposed.

In the course of optimization of conditions of methylmercury deposition following parameters were studied: pH of supporting electrolyte, concentration of DTPA, accumulation time and influence of Hg(II) concentration on methylmercury peak current. At optimized conditions methylmercury was determined in the range from 1×10^{-8} to 5×10^{-7} M in the presence of 2.5×10^{-5} M Hg(II). Interference of chlorides and nitrates on analytical signal of methylmercury was studied because HCl and HNO₃ are often used to extract methylmercury from solid samples.

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PP-18**DETERMINATION OF NICKEL BY ADSORPTIVE STRIPPING VOLTAMMETRY AT AN *IN SITU* PLATED BISMUTH FILM ELECTRODE****MIECZYSLAW KOROLCZUK, IWONA RUTYNA, MALGORZATA GRABARCZYK, KATARZYNA TYSZCZUK**

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Adsorptive stripping voltammetry has been established as a reliable trace metal analysis in cases, where the analyte forms intermetallic compounds or cannot form an amalgam, as *e. g.* Ni, Co or Cr. Procedures for these ions determination rely on interfacial accumulation of complexes of the target metals onto the working electrode and then reduction of the accumulated complex. In the case of Ni(II) determination, complexes with dimethylglyoxime or nioxime were most commonly exploited. Although reports on Ni(II) or Ni(II) and Co(II) determination at a bismuth film electrode can be found in the literature in all reported procedures, the electrodes were plated *ex situ*.

In this communication we present the procedure for Ni(II) determination by adsorptive stripping voltammetry in the presence of nioxime at *in situ* plated bismuth film electrode. For stabilization of Bi(III) added to the sample solution tartrate was introduced to the supporting electrolyte. It must be noted that Bi(III) should be added to the solution as its complex with tartrate to avoid its hydrolysis at mild alkaline conditions.

Taking into account the fact that in the proposed procedure for the first time the bismuth film electrode is plated *in situ* from a mild alkaline solution, to pH of 10, the optimization of conditions of plating bismuth film and Ni(II) determination was performed. At optimized conditions the calibration graph for the accumulation time of 120 s was linear from 5×10^{-9} to 5×10^{-8} M.

Two ways of regeneration of the electrode after measurements were studied and it was found that the best way of regeneration leading to reproducible results rely on reduction of accumulated metal ions to metallic state at -1.1 V.

Possible interferences by metal ions and surfactants were studied. The proposed procedure was validated by analysis of water certified reference material.

PP-19
PROPERTIES OF ION-SELECTIVE ELECTRODES
WITH POLYMERIC MEMBRANES
FOR KETOPROFEN DETERMINATION

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Ketoprofen, 3-benzoyl- α -methylbenzeneacetic acid is used in medicine as an analgesic and anti-inflammatory drug¹. So far a number of methods of quantitative determination of ketoprofen have been applied, but they are relatively complicated, expensive and require a time-consuming preparation of a sample to analysis. Therefore, new methods are being developed, including potentiometric methods with ion selective electrodes used.

The aim of the research was to create the electrodes based on PVC membrane which are indirect contact with an Ag/AgCl electrode. The electrodes have not any inner solution and they possess all the advantages of the “coated wire electrodes”. The detailed construction of the electrode was described in earlier paper². The membranes were plasticized with bis(2-ethylheksyl)sebacate, dibutyl phthalate, diisobutyl phthalate, tris(2-ethylheksyl) phosphate, 2-nitrophenyloctyl ether in which the active substance tetraoctylammonium 3-benzoyl- α -methylbenzeneacetate was dissolved.

The basic analytical parameters of the ketoprofen electrode like: measuring range, detection limit, response time, life time, and selectivity coefficients for some organic and inorganic anions were determined. The electrode was used to determine ketoprofen in synthetic sample and pharmaceutical preparations in injections, tablets and capsules. The examined electrodes can be applied to ketoprofen determination in the concentration range of 25–25 000 $\mu\text{g mL}^{-1}$ in water solution at pH 5.5–8.5. The statistical parameters (recovery 99–102 %, RSD < 3 %) indicate the typical accuracy of the analytical methods employing ion-selective electrodes.

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PP-20
ELECTROCHEMISTRY OR AAS FOR TRACE
ANALYSIS OF METALS

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Trace concentrations of metals are usually determined by atomic spectrometry, mostly by graphite furnace atomic absorption spectrometry (GF AAS) and mass spectrometry with inductively coupled plasma ionisation (ICP MS). The superior selectivity, sensitivity and broad availability of the AAS method makes it usually the choice No 1 when seeking for a method for trace concentrations. Electrochemical methods also facilitate trace analysis of metals but cannot compete spectrometric methods owing to lower selectivity, limited number of metals measured, laborious and tedious procedures. Yet, in some cases electrochemical methods may reasonably complement or even exceed AAS:

1. analysis of samples with high salt contents for easily evaporating elements such as Hg, Cd, Pb, *etc.*,
2. determination of some semimetals such as As, Se, Sb,
3. speciation analysis, *e.g.* As(III)/As(V), Cr(III)/Cr(VI),
4. on-line process analysis where atomic spectrometers could hardly be employed.

Moreover, electrochemical sample pre-treatment can significantly improve the performance of AAS in special instances:

1. hydride forming elements can electrochemically be converted to the corresponding hydrides and measured by AAS,
2. metals and semimetals can be electrochemically preconcentrated on large surface electrodes and on stripping measured by GF AAS. In such a way matrix effects can be minimised and detection limits improved.

The purposes of the methods for metal preconcentration are often different, depending on whether the methods are applied in environmental or another field. The respective method needs to be efficient, give high sensitivity and selectivity, which is useful when used in combination with atomic spectrometry techniques. Preconcentration procedures are considerable tools in analytical processes, since their applications guarantee trace metal analyses in complex matrices and improve the performance of the analytical techniques. Moreover, the preconcentration procedures exploiting the clean chemistry concept and the reduction of samples/reagents consumption are extensively used. In this contribution the brief descriptions of the methods for preconcentration procedures related to electrochemical deposition are discussed, as well as some applications are presented.

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PP-21

QSER OF 1-ARYL-5-BENZYL-SULPHANYL-TETRAZOLES AND THEIR ELECTROOXIDATION AS A METABOLIC MODEL

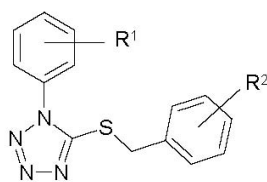
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It is known, that the methods of quantitative structure-property and structure-activity relationships (QSPR/QSAR) are widely employed in the development of new pharmaceuticals. Recently, the term “quantitative structure-electrochemistry relationships” (QSER) has been adopted in the case of QSPR where the electrochemical properties (*e. g.*, half-wave potential, energy of HOMO) are correlated¹. Electrochemical methods are useful tools not only for investigation of electron-transfer reactions but they can provide valuable information that helps understand some of the biological reactions, *e. g.* drug biotransformation².

One of the significant directions of current pharmaceutical chemistry is the search for new antimycobacterially active compounds. Proceeding in our previous study³, we synthesized a new group of promising agents: 1-phenyl-5-benzylsulphanyltetrazoles.

In the first part of this paper, QSER of nineteen benzylsulphanyltetrazoles are reported. The second part of the work is concerned on preparative electrolysis and identification of oxidation products as a model for metabolic oxidation of studied compounds.



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PP-22

APPLICATION OF THE AMORPHIC TiO₂ IN VOLTAMMETRIC ANALYSIS

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Absorption of surface active substances (SAS) on a working electrode in voltamperometric techniques causes decrease or even diminishing of the analytic signal. Therefore, while using natural samples, specific pretreatment procedures are required.

One of the methods eliminating SAS-related influence on the measurement consists in addition of the fumed silica directly to the electrochemical cell^{1,2}.

In this paper it is suggested to replace fumed silica with titanium dioxide.

In an experiment the following chemical compounds were used: two forms of titanium dioxide (crystalline – anatase and amorphous – technically known as P-25 Degussa®), dodecylbenzenesulfonic acid sodium salt, hexaacyltrimethylammonium bromide and humic acids (Fluka Chemie GmbH) as SAS. SAS sorption on the titanium dioxide was estimated by a differential double-layer volume technique and a stripping-voltammetry.

As a result it was proven that:

1. Titanium dioxide added directly into the measuring cell in its amorphous form of P25 (50 mg/10 mL) is much more effective in removing of humic acids, than crystalline form of titanium dioxide.
2. Sonification in the presence of P25 improves its effectiveness as humic acid sorbent (sonification without P25 is not so efficient).
3. Application of UV radiation increases P 25 sorption effectiveness and enables elimination of higher humic acids concentrations (up to 20 ppm).
4. In the presence of humic acids the addition of P25 improves depolarizer signal in voltammetric analysis.
5. Addition of 50 mg of P25 directly to the voltammetric cell causes decrease of depolarizer analytic signal by 3%, what suggests its sorption on titanium dioxide.

The study was financed by the Polish Ministry of Science and Education No. 18.18.160.579.

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PP-23**KAOLIN ROCKS AS ADSORBENT OF THE NON-IONIC SURFACTANT****EWA NIEWIARA, WITOLD RECZYŃSKI, WŁADYSŁAW W. KUBIAK**

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Certain amount of samples analyzed by means of voltammetry is contaminated with the surface active substances (SAS). It induces application of the sample pre-treatment procedures. In the former papers, application of fumed silica as SAS adsorbent was described^{1,2}. Herein, the use of some natural minerals – kaolin Osmoza, kaolin Imperial and kaolin Le Extra – as non-ionic SAS Triton X100 (TRT X100) adsorbents was examined. The results were related to the sorptive properties of fumed silica and cadmium ions were used to indicate sorption efficiency of the listed above adsorbents. From 80 mg to 500 mg of minerals per 10 mL of solution were added directly into the electrochemical cell. The stripping voltammetry technique was used for Cd concentration measurements.

It was found that:

1. The highest sorption efficiency of non-ionic SAS exhibited kaolin Osmoza.
2. At the same instant, depolarizer was most effectively adsorbed from the solution with 400 mg of kaolin Osmoza added.
3. Kaolin Osmoza may be used for the removal of non-ionic SAS up to its concentration of 2.5 ppm. Addition of 80 mg of kaolin to 10 mL of solution is needed.
4. The examined kaolin minerals were not selective, *i.e.* they adsorbed both – SAS and depolarizer ions.
5. Kaolin Le Extra was of no analytical use.

The study was supported by Ministry of Education and Science (AGH University Project No.11.11.160.799).

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PP-24**ADSORPTION OF METHIONINE AT A MERCURY/AQUEOUS SOLUTION OF NaClO₄ INTERFACE; DEPENDENCE ON THE SUPPORTING ELECTROLYTE CONCENTRATION****AGNIESZKA NOSAL-WIERCIŃSKA, GRAŻYNA DALMATA**

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Methionine is an essential α -amino acid containing sulphur. It is indispensable to the correct functioning of organisms. Methionine has found a wide use in medicine for its detoxication, anti-inflammatory and antidepressant applications. It also enhances the pharmacological performance of lithium, antibiotics and sulfamides. Apart from that it has also been found a Bi(III) ions electroreduction catalizer¹. Methionine adsorption on the mercury/chlorate(VII) interface was examined in 0.5 M to 8 M chlorate(VII) solutions. The course of the differential capacity curves on mercury (Cd) in 0.5 M to 8 M chlorate(VII) solutions containing $0.5\text{--}50 \times 10^{-3}$ M methionine indicate a methionine adsorption on mercury/chlorate(VII) interface. With the increase of methionine concentration the hump appearing on the $C_d = f(E)$ curves decreases and shifts towards the negative potentials. The same effect is observed with the increase of chlorate(VII) concentration in non-methionine containing solutions. The linear dependencies the potential of zero charge from methionine concentration obtained for all the examined chlorate(VII) concentrations point to a specific methionine adsorption on mercury electrode. Methionine relative surface excesses (Γ') were determined at constant electrode charge². The surface excess values increase with increasing methionine concentration and electrode charge. The surface excess depends on the supporting electrolyte concentration. Along with the chlorates (VII) concentration increase from 0.5 M to 3 M methionine surface excess values rise in the electrode charge range from -8×10^{-2} C m⁻² to $+13 \times 10^{-2}$ C m⁻². In 4 M and 5 M chlorates (VII) a considerable value decrease appears in methionine surface excess. A further base electrolytes concentration increase causes a slight surface excess value rise. The highest surface excess values were obtained in 3 M chlorates(VII). In methionine adsorption description the following isotherms were used: Frumkin, Viral, modified Flory-Huggins isotherm. Energy adsorption and constant interactions between the already adsorbed methionine molecules were appointed. The adsorption parameters change in the base electrolytes function point to a competitive methionine molecules and ClO₄⁻ ions adsorption as well as to a electrostatic interaction between methionine and water molecules.

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PP-25
ELIMINATION VOLTAMMOGRAMS
OF MINIATURIZED MERCURY DROP ELECTRODES

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Elimination voltammetry with linear scan¹⁻⁴ in connection with renewed stationary mercury electrodes (HMDE/SMDE) can provide valuable information about nature and kinetics of processes at electrode interfaces. Its application is based on the unique treatment of voltammetric current-potential dependences measured at certain scan rates. In common cases the size of the HMDE does not change. Recent development of miniaturized mercury electrodes (MME) has brought much broader range of their accessible geometrical parameters⁵⁻⁹. Preliminary DC-voltammetric measurements using MME revealed the effect of its size on the shape and course of the measured peaks.

The aim of this study was to measure DC-voltammograms under controlled conditions using stationary mini- or semimicro-drop electrodes with different diameters and to apply corresponding elimination procedures. Procedures of preparation of the mentioned types of sensors were described. As it was expected, the course and parameters of the obtained elimination voltammograms depended on the size of the miniaturized renewed stationary mercury drop electrodes.

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P-26
RECENT PROMISING MINIATURIZED RENEWED
MERCURY OR RELATED ELECTRODES
AND PLASTIC SENSORS

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Renewed mercury and related electrodes still maintain¹⁻⁸ nowadays, almost 90 years after the discovery of polarography and 50 years after the award of Nobel prize to professor Jaroslav Heyrovský, their irreplaceable importance in physico-chemical, electrochemical and electroanalytical research and in the therewith connected wide practice.

Recently²⁻⁸ new types of mercury, amalgam and composite amalgam sensors or analogously arranged sensors based on various other materials (of adequate rheological behaviour – liquids, pastes, mixtures, composites, gels, inks, solids) have been designed. For example³⁻⁷, the attention has been paid to miniaturization as to their size or amount of active phase from mini-, semimicro-, micro- to nanolitre scale (mS, μ S, μ S to nLS/nVS-sensors or elodes mE, μ E, μ E, nLE/nVE); to capillary or plastic-tip sensors/elodes (PTS/E); to renewable forms [drops (DE), meniscus (ME) or hemisphere (HE)] and modes like DME, HMDE, SMDE, SMME, HMHE, ... elodes or DE, sME, or sHE incl. their staircase increasing/decreasing size, contraction/expansion, etc.; to their various materials (organic, inorganic, bio-), various arrangements of sensors, systems, pulse generators producing proper sequence of pulses, satellite control or monitoring, etc.

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PP-27
EFFECTS OF ELECTROLYTES ON THE NOISE
IN THE OVER-LIMITING CURRENT RANGE

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This research work investigates the i - v and V - t curves, particularly the effect of the counter ion nature on the noise in the over-limiting current I_{ov} . The overlimiting current is always accompanied by a neat electrical noise. It is a well accepted experimental phenomenon¹⁻⁵. The study of this may contribute to a better understanding of the I_{ov} nature and the water dissociation mechanism.

This research work presents original finding: The electrical noise depends directly on the counter ion nature. The noise intensity decreases according to the Hoffmeister series: $Li^+ > Na^+ > K^+$. We explain this by the hydration number of the counter-ion. The ion NH_4^+ presents a singular behavior; the noise is minimal.

We are most grateful to Prof. Benachour Djaffer (Algeria), Prof. Tahar Bendaikha (Algeria), Prof. Saidani Boualam (Algeria), Prof. C. Gavach (France), Dr. F. Lutin (EURODIA, France), Prof. J. Benavente (Spain), Prof. Seung Hyeon Moon (Korea), Prof. Hubert Giraut (Lausanna), Dr. Maarten Van Brussel (The Netherlands).

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PP-28
THE CHEMICAL INVESTIGATING METHODS
OF CONCENTRATION POLARIZATION
IN ELECTRODIALYSIS

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This research work investigates the i - v and v - t curves, particularly the physical meaning of the plateau length of the limiting current I_{lim} and the nature of the over-limiting current (I_{ov}). In recent papers¹ Wessling *et al.* presented I_{ov} as a puzzle and a non elucidated problem. They concluded that electro-

convection, theory proposed by Rubinstein, explains I_{ov} . Our research team has developed original experimental methods to investigate the i - v curve and related problems:

- The buffer solutions method²: $HPO_4^{2-}/H_2PO_4^-$ used as co-ions or counter-ions^{3,4}.
- The weak electrolytes method^{3,4}: the addition of phenol, boric acid.

We consider that these experimental results constitute clear and strong contributions to the i - v curve understanding and cannot be explained by electro-convection. Today we confirm this approach by new experiments which combine both properties: the buffer is NH_4^+/NH_3 and the neutral weak electrolyte is NH_3 . Our experiments have been obtained automatically (AutolabPGSTAT30) and manually with classical membranes (CMV, CMX) and a free convection four electrodes cell.

We explain these results by the change of the dielectric properties of the membrane inside. Under the effect of very high local electric field (space charges), the pK_a of weak electrolytes is lowered (Wien effect and Booth equation) which improves the membrane conductivity. These phenomena explain I_{ov} . Our discussion will be based on the effects of weak electrolyte pK_a values and concentrations. The research works of Pintauro *et al.*⁵ and Tanioka⁶ constitute a strong literature confirmation of our new chemical experimental approach.

We are most grateful to Prof. C. Gavach (France), Dr. F. Lutin (France), Prof. Seung Hyeon Moon (Korea).

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PP-29
MODELLING OF WATER TRANSPORT IN
A PROTON EXCHANGE MEMBRANE FOR FUEL
CELL (PEMFC) EFFECTS OF POROSITY

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A model of water transport in a membrane electrode assembly (MEA) of a proton exchange membrane fuel cell is developed. The model takes into account, diffusion, migration, convection, and drags in the membrane phase and considers the membrane as a proton structure a porous structure. The mathematical model is solved using finite element tool. In this paper we had calculated and discussed one dimensional distribution of water in the cell with and without porosity.

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PP-30**ELECTROCHEMICAL SENSORS FOR HYDROPEROXIDES IN WATER AND ACETONITRILE**

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Electrochemical catalytic effects can be a valuable analytical tool for determination and detection of many analytes. We have found that in water during electroreduction of Fe(III) in the presence of HOOH and *t*-BuOOH, cathodic catalytic currents could be registered, whereas in acetonitrile electrooxidation of Fe(II) in the presence of mentioned hydroperoxides gave anodic catalytic currents (where hydroperoxides acted as reducing agents)¹.

In present research cyclic voltammetry was used to investigate the electrochemical properties of modified GCE electrodes. The possibilities of obtaining the sensors for *t*-BuOOH and HOOH determination, working on the basis of electrochemical catalytic currents were considered. Immobilization of the catalyst onto the surface of the electrodes prevents contamination of the analytical sample. The electrodes under study were GCE modified with the Nafion doped with Fe(III) and GCE, modified with polyaniline, poly(*N*-methylaniline) and poly(*N,N*-diethylaniline), doped with Fe(II).

GCE/Nafion, Fe(III), electrode were proved to be useful for construction of disposable, sensitive sensors for HOOH and *t*-BuOOH in water. GCE/poly(*N,N*-diethylaniline), Fe(II); GCE/polyaniline, Fe(II); GCE/poly(*N*-methylaniline), Fe(II) electrodes can be used for construction of stable, reusable sensors for determination of HOOH and *t*-BuOOH in acetonitrile.

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PP-31**THE CORRELATION OF SODIUM, POTASSIUM, CALCIUM AND MAGNESIUM IONS IN HUMAN ORGANISM STUDIED BY POTENTIOMETRIC AND SPECTROFOTOMETRIC METHODS**

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Magnesium as well as a number of other monovalent and divalent bioelements like sodium, calcium plays an important role in a proper work of whole chain of intracellular metabolism^{1,2}.

The aim of this job was determination of current contents of some bioelements (potassium, sodium, calcium and magnesium) in blood of randomly chosen age population *i.e.* 9th to 75th year of life and their statistic interpretation in relation to common interrelation.

A content of elements was determined using the method of spectofotometric and potentiometric. The values of obtained concentration of the determined bioelements have been drowning up according to the applied division into two groups (male and female). The obtained results were subjected to statistic analysis.

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PP-32**POTENTIAL-TIME RESPONSE OF BIOMIMETIC MEMBRANES IN PRESENCE OF ZINC AND MAGNESIUM IONS**

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It was recently shown that the conducting polymer (CP) films doped with biologically active ligands may be used as model biological membranes to study the mechanism of mem-

brane potential formation¹. In particular the CP films may be used to study competitive binding of cations to biologically active ligands such as adenosine triphosphate (ATP) and resulting impact on transient membrane potential during equilibration.

In this study the interaction of magnesium/zinc ions with ATP was in focus. ATP is the universal energy currency for all known life forms. ATP and its reaction products provide or store energy for all organism activity. All the enzymatic reactions of ATP require the presence of metal ions able to interact with the nucleotide to form complex molecules that act as the real substrate. ATP-Mg species often accomplish this role, however other cations such as Zn(II), Cu(II), Mn(II) and Al(III) are of much importance for the biochemistry of ATP, and for toxicity effects related to interference in ATP-associated reactions^{2,3}.

The ATP ions were introduced into poly(pyrrole) and poly(3,4-ethylenedioxythiophene) films during electropolymerization. The CP films were conditioned to allow for the admission of Zn²⁺ or Mg²⁺. The films sensitive for Zn or Mg ions were used as model membranes in potentiometric measurements. Close-to-Nernstian sensitivity was observed for the films under equilibrium. During equilibration, provoked by the change in concentration of Zn²⁺ or Mg²⁺, a characteristic, and distinctively different for Zn and Mg ions, transitory potential response was observed. This behaviour is ascribed to the surface concentration changes of Zn and Mg due to the competitive binding at the ATP membrane sites during equilibration.

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PP-33

ARRANGEMENTS OF PLATINUM ELECTRODES IN AMPEROMETRIC DETECTORS FOR DETECTION OF HYDROXY AND AMINO DERIVATIVES OF POLYCYCLIC AROMATIC HYDROCARBONS

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The development of amperometric detection in liquid flow methods represents one of the most active and successful movements in electroanalytical chemistry. Among variety of materials used, platinum indicator electrodes remain popular

due to their sensitivity, mechanical robustness, easy of electrochemical pretreatment and geometry variability¹.

This study compares two arrangements of platinum indicator electrode in home-made amperometric detectors. They consist from the pen-type reference and auxiliary electrodes placed in an overflow vessel close to Teflon tubing (1/16" o.d., 0.010" i.d.) joined to the column outlet. This tubing accommodates the Pt indicator electrode: The platinum tubular electrode (effective area 0.6 mm²; ref.²) or the platinum microcylindrical electrode (geometric area 0.08 mm²) made by fixing of a thin platinum wire in the Teflon tubing across to the flow of mobile phase.

Both detectors were employed for the detection of selected hydroxy and aminoderivatives of polycyclic aromatic hydrocarbons (naphthalenes, biphenyls) after their HPLC separation using reversed C₁₈ phase and phosphate buffer – acetonitrile mobile phase. The Pt tubular detector is more sensitive with detection limits typically in the 10⁻⁸ M concentration range, while the Pt microcylindrical detector (detection limits typically in the 10⁻⁷ M concentration range) has the advantage of lower peak tailing, which would be covetable for analysis of more complicated mixtures. The reproducibility of the detector response is satisfactory in both cases even for aminonaphthalenes that are known to form polymerizing films as products of oxidation at platinum or carbon electrodes leading to electrode fouling.

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PP-34

COPPER AMALGAM ELECTRODES IN THE DETERMINATION OF ARSENIC, SELENIUM AND ELEMENTAL SULFUR

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The most of arsenic forms and compounds are very toxic and cancerogenic. Arsenic toxicity depends on its speciation *i. e.* compounds of As(III) are much more toxic than compounds of As(V). Considering the very low concentration limits of arsenic acceptable in the environment, drinking water, food and similar products¹. Selenium is an important element in biological and environmental systems. Selenium is an essential trace element in human body. A lack or excess of selenium leads to several disease. In case of selenium gap

between toxic concentration and concentration as bioelement is very narrow². Thus a sensitive method of determining selenium and arsenic are necessary.

Elemental sulfur, S(0) is formed during the biotic and abiotic oxidation of dissolved sulfide and solid metal monosulfides. The data available on their amounts in marine pore waters are limited, and there is practically no data for pore waters of freshwater systems³. This lack of data is the result of a paucity of reliable analytical methods that could be used to determine low concentrations of elemental sulfur.

In the work the determination of trace arsenic, selenium and elemental sulfur were carried out using differential pulse cathodic stripping voltammetry (DPCSV) at the copper amalgam electrodes. The proposed method is easily optimized. The detection limit for As(III) as low as 25 ng L⁻¹ (preconcentration time (240 s) for Se(IV) as low as 20 ng L⁻¹ (preconcentration time 120 s) and for S(0) as low as 14 ng L⁻¹ (preconcentration time 60 s) could be obtained.

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PP-35

APPLICATION OF THE ELECTRODE TYPE Hg(Ag)FE IN THE DETERMINATION OF MOLYBDENUM, MANGANESE AND SELENIUM

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Most voltammetric methods required mercury electrodes. The Hanging Mercury Drop Electrode (HMDE) is the electrode of preference due to its high sensitivity, reproducibility and linearity. However, the toxicity of mercury limits the usage of the mercury electrodes in the analytical practice and excludes them from the out-of-laboratory applications. The problem of limiting the amount of mercury or its soluble salts needed for the analytical procedure can be solved with the help of a Renewable Silver Amalgam Film Electrode (Hg(Ag)FE). The principle of working and first proposal of a Hg(Ag)FE electrode construction was made by Baś and Kowalski¹. The construction the cyclic renewable mercury film electrode is depicted on Fig. 1.

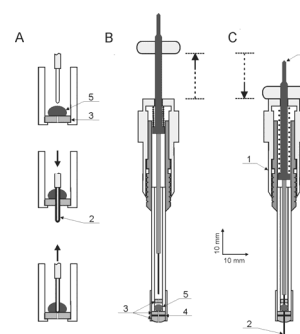


Fig. 1. The principle of mechanical refreshing of the mercury film silver based electrode. The Hg(Ag)FE used in our experiments: (1) micrometric screw, (2) piston pin with Ag cylindrical electrode at the end, (3) O-ring, (4) Ag foil (0.05 mm), (5) liquid Ag amalgam (~10 µl), (6) electric contact pin

The Hg(Ag)FE refreshed before each measurement demonstrates many properties which are specific only to the hanging mercury electrode²⁻⁴. The preparation of the Hg(Ag)FE is very simple and regeneration of the mercury film is easy and very short. The Hg(Ag)FE was successfully applied for the determination of Mo, Mn and Se.

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PP-36

ELECTROCHEMICAL DETERMINATION OF DICLOFENAC SODIUM IN AQUEOUS SOLUTION ON Cu-DOPED ZEOLITE – EXPANDED GRAPHITE-EPOXY ELECTRODE

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Diclofenac is a common anti-inflammatory drug. In recent years, pharmaceutical drugs constitute a novel class of water contaminants¹⁻⁴, and their determination by a fast and simple method is necessary.

An electrochemical sensor based on Cu-doped zeolite-modified expanded graphite-epoxy composite electrode was evaluated for a new alternative of quantitative determination

of sodium diclofenac in aqueous solutions. Cyclic voltammetry was used to characterize the electrochemical behaviour of the electrode in the presence of sodium diclofenac in 0.1 M Na₂SO₄ and 0.1 M NaOH supporting electrolyte. This modified electrode exhibited electrocatalytic effect towards sodium diclofenac oxidation, allowing its determination in aqueous solution. The linear dependence of the current versus diclofenac concentration was reached using cyclic voltammetry, differential-pulsed voltammetry, and chronoamperometry.

Substantial enhancement of electrode sensitivity for the determination of sodium diclofenac at Cu-doped zeolite-modified expanded graphite-epoxy composite electrode was reached by applying a chemical preconcentration step prior to voltammetric quantification. Also, under these last conditions better the lowest limit of detection was achieved, allowing the analytical utility of this electrode over a concentration range where aquatic sodium diclofenac pollution is known to occur.

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PP-37

ELUCIDATION OF ELECTRODE REACTION MECHANISMS BY DIFFERENTIAL PULSE POLAROGRAPHY

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The use of computers in the control of the experiments was a key factor for the rebirth of polarographic techniques in the 90's decade. From the discovery of d.c. polarography by J. Heyrovsky, other techniques were developed such as fast, normal pulse, NP, differential pulse, DPP, or a.c. polarography. DPP is a widely used electroanalytical technique because the decrease in the charging current's relative contribution of the measured current. The DPP parameters that can be changed are the pulse amplitude and the pulse duration. The selectivity and sensibility of the technique can be increased by controlling both parameters. But DPP can be also used in electrode kinetics, and the aim of this communication is to show its utility in this task.

Though equations obtained from rigorous theoretical treatments are difficult to handle to obtain kinetic parameters,

approximate equations were developed, allowing the kinetic analysis¹⁻⁷. By exploring the different parameters of the technique, DPP can be used for the elucidation of the kinetics of the electrochemical processes (with the evident exception of the product and intermediate identification). So, the type of transport (diffusional or chemical) can be evidenced from the dependence of the currents with the pulse amplitude⁴, the electrochemical reaction order with respect the electroactive species from the shape of the polarogram^{1,2,5}, the type of rate-determining step from the dependence of the peak potentials on the pulse duration⁴, the electrochemical reaction order with respect other species, such as the H⁺ ion, from the dependence of the peak potentials on their concentrations^{1,2,4,5,7} etc.

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PP-38

ELECTROCHEMICAL CATALYTIC CURRENTS FORMED IN THE PRESENCE OF DIOXYGEN AND TRANSITION METAL COMPLEXES OF SALEN

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The mechanism of activation of dioxygen by means of transition metal complexes is very important in many aspects of chemical study as well as biological transformations. In these processes the intermediates with incorporated oxygen are formed¹⁻³. They can be a source of oxygen in the reaction of oxidation of organic compounds, and can substitute classical oxidants *i. e.* heavy metal salts. Understanding of dioxygen activation mechanism will lead to development in many fields connected with „Green Chemistry”, waste products management, and biochemical reactions occurring in living organisms^{4,5}.

Recently we have found that in acetonitrile, [Fe^{II}(salen)]_{solv} is rapidly oxidized by dioxygen to give Fe(III) complex. The exposition of the solution to air or dioxygen atmosphere causes the complete oxidation of [Fe^{II}(salen)]_{solv}. Electro-

chemical reduction of $[\text{Fe}^{\text{III}}(\text{salen})]^{+\text{solv}}$ formed, causes the increase of observed current, which indicates that the catalytic process occurs and reactive oxygen species are formed during that processes. It is very interesting that the observed increase of the catalytic current is the same in the presence of dioxygen and air. We also tried to employ preparative electrochemical reduction of system containing $[\text{Fe}^{\text{III}}(\text{salen})]^{+\text{solv}}$ and dioxygen to oxidation of unsaturated hydrocarbons. This attempts were unsuccessful due to the deactivation of electrode surface by decomposed complex. However, we have found that metal-salen complexes activate dioxygen for oxidation of unsaturated hydrocarbons.

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PP-39

Zn²⁺ ELECTROREDUCTION MECHANISM AT MERCURY INTERFACE/CONCENTRATED NaClO₄ SOLUTIONS IN THE PRESENCE OF TETRAMETHYLTHIOUREA

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Based on the literature¹ we know that the increase of NaClO₄ concentration from 0.2 M to 7.0 M causes an increase of the true standard rate constants, k_f^1 for Zn²⁺ ions reduction, but only for NaClO₄ concentration ≥ 1.0 M. We showed² that the catalytic activity of tetramethylthiourea (TMTU) decreased in the order 1.0 M NaClO₄ > 0.5 M NaClO₄ > 0.1 M NaClO₄. The studies on adsorption and catalytic activity were carried out in NaClO₄ solutions of the following concentrations: 2 M, 3 M and 4 M. The relative surface excess values of TMTU increased with the increase of NaClO₄ concentration. The obtained k_f^1 values for Zn²⁺ ions reduction in the presence of TMTU in 2 M, 3 M and 4 M NaClO₄ were distinctly higher than for diluted solutions. In diluted NaClO₄ solutions a distinct acceleration effect rise appeared in the true standard rate constants values, which characterizes the first electron transfer stage and the second electron exchange stage². In the currently studied systems, the second electron transfer stage maximum value rise, practically did not depend on the base electrolytes concentration. This may be the result of a similar Zn²⁺ aquaion composition.

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PP-40

ADSORPTION OF TETRAMETHYLTHIOUREA AT MERCURY ELECTRODE IN THE PRESENCE OF 1-DECANESULFONIC ACID

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The following study describes 1-decanesulfonic acids and tetramethylthiourea (TMTU) adsorption process at mercury electrode in 1 M NaClO₄. In this process the first substance adsorbs physically at mercury electrode whereas the second one undergoes chemisorption. After adding TMTU to the solution containing 7.5×10^{-4} M 1-decanesulfonic acid the following reactions were observed: an increase of differential capacity, a distinct formation of TMTU desorption peaks, a significant surface tension decrease and a zero potential charge shift towards more negative potentials. The TMTU molecule occupied 0.152 nm² of the surface which was a considerably smaller amount than in the absence of the detergent. The *A* interaction constants obtained from Frumkin and Flory-Huggins isotherms point to a weak repulsive interactions between the TMTU molecules, which rise towards more negative electrode potentials. The ΔG° adsorption energy increases with the rise of electrode charge, however its adsorption energy increase is smaller compared to the ones in the absence of the detergent¹. Inner layers electrostatic parameters were determined using Parsons' electrostatic model². A dependence between all electrostatic parameters and electrode charges was proven.

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PP-41**ADSORPTION OF 1-DECANESULFONIC ACID AT MERCURY ELECTRODE IN 1M NaClO₄ SOLUTION****DOROTA SIENKO, JADWIGA SABA, MAŁGORZATA KLIN, JOLANTA NIESZPOREK, DOROTA GUGAŁA-FEKNER***Faculty of Chemistry, M. Curie-Skłodowska University, M. Curie Skłodowska Sq. 3, 20-031 Lublin, Poland
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1-Decanesulfonic acid is a biological detergent used to separate nucleic acids and proteins from their cellular structures. The adsorption studies were carried out below critical micellar point. The detergent concentration increase not only caused a distinct differential capacity and surface tension decrease but also a zero charge potential shift towards less negative potentials. The maximum adsorption¹ of 1-decanesulfonic acid appeared at -0.463 V potential and at $q = 0$ electrode charge. The adsorption parameters were determined using Frumkin and Flory-Huggins² adsorption isotherms in the electrode charges range from $-2 \mu\text{C cm}^{-2}$ to $+2 \mu\text{C cm}^{-2}$. The conducted studies found that for $q = 0$ the weakest repulsive interactions between 1-decanesulfonic acid ions occurred and that the free ΔG° adsorption energy reached its greatest value. The obtained adsorption parameters justify 1-decanesulfonic acid greatest value of surfaces excess for $q = 0$.

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PP-42**GLASSY CARBON ELECTRODES MODIFIED WITH PEDOT/PSS: OPTIMIZATION STUDIES FOR TRACE LEAD DETECTION****CARLA P. SILVA, JOSÉ P. PINHEIRO***Department of Chemistry/CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
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The polyelectrolyte poly(sodium 4-styrenesulfonate), PSS has already been successfully used to coat a glassy carbon/thin mercury electrode (GC/TMFE) and applied to the square-wave anodic stripping voltammetry (SWASV) of trace metals^{1,2}. However, it still needs an optimization in order to present the better relation between a high density of $-\text{SO}_3^-$ groups on the deposited coating and low leakage of this coating to the test solution, consequently broadening the voltammetric signal². On the other hand, the conducting polymers are often fruitfully employed as redox-mediators towards several analytes, significantly enhancing sensitivity and selectivity of the analytical detection and even lowering the detection limit³. PEDOT is considered the most stable conducting polymer currently available, being especially attractive when high stability of the polymeric material is required⁴.

PEDOT-PSS complex is the most widely utilized because it has a good shelf life, can be easily coated on various substrates to form thin films by many methods, thus showing good film-forming properties, and displays an excellent stability^{5,6}. PEDOT-PSS composite films behave as a cation exchanger⁷.

In the present study, the incorporation features of such PEDOT-PSS coatings towards lead(II) accumulation in the polymer film are optimized regarding some features like: scan rate used for the electropolymerization, number of scans, EDOT:PSS ratio present in the electropolymerization solution. The stability reproducibility and repeatability of the selected coating of PEDOT-PSS were also evaluated.

Thanks are due to "Fundação para a Ciência e Tecnologia" (FCT) for financial support (Project POCI/AMB/55939/2004).

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PP-43**KINETICS OF HETEROGENEOUS ELECTRON TRANSFER REACTIONS IN IONIC LIQUIDS****NOUREEN SIRAJ, GÜNTER GRAMPP, STEPHAN LANDGRAF***Institute of Physical and Theoretical Chemistry, Graz University of Technology, Technikerstrasse 4/I, A-8010 Graz, Austria
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Heterogeneous electron transfer rate constants, k_{het} , of organic molecules have been measured by cyclic voltammetry in three different room temperature ionic liquids (RTILs): [emim][BF₄], [bmim][PF₆] and [bmim][CF₃SO₃]. Various organic acceptor (A) and donor (D) systems:



like ferrocene, chloranil, bromanil, methylviologen (MV), ethylviologen (EV), tetracyanoethylene (TCNE), *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPPD), tetrathiafulvalene (TTF) and *p*-phenylenediamine (PPD) are used. The

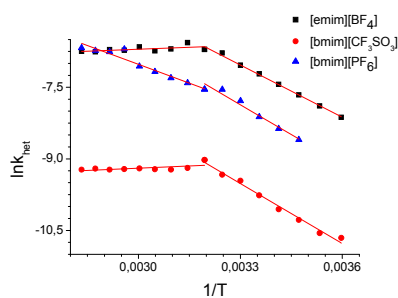


Fig. 1. $\text{Fe}(\text{cp})_2$ in three different RTILs

results obtained in RTILs are compared with those found in organic solvents, like CH_3CN etc.¹. Diffusion coefficients have been calculated in these ionic liquids and have also been compared with those found in classical organic solvents². They depend on the inverse viscosity for all molecules under investigation. An interesting behavior has been observed in RTILs while plotting $\ln D$ against $1/T$. This Arrhenius plot shows two different linear slopes with transient temperature of 313K (almost) for all three RTILs. Although few temperature studies in RTILs has been reported in literature but this two different slope trend has not been mentioned over there³. The same behavior was also observed when plotting $\ln k_{\text{het}}$ versus $1/T$ using Marcus equation. These two different linear slopes results in two different values of activation energy for the electron transfer. The main problem arising here to understand the role of λ_0 which is describe by dielectric constant ϵ_s and a refractive index n . Such a concept is not applicable to the charged ions of the ionic liquids acting as solvents.

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PP-44

FASTER VOLTAMMETRIC ASSAY OF WATER SOLUBLE PHTHALATES IN BOTTLED AND COOLER WATERS

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Phthalic acid and phthalates esters are of growing interest due to their significant use and potential toxicity. A faster, simpler and highly sensitive Square Wave Voltammetric (SWV) method was developed for evaluation of total water soluble phthalates by taking 95% aqueous di-*n*-butyl phthalate (DBP) as a model at glassy carbon electrode. The study showed that 100 μM aqueous solution of DBP gives best response with 0.05 M tetrabutylammonium bromide, at stirring rate of 1400 rpm, deposition time, 20 s and pH 4.0. The optimum frequency and scan rate was 100 Hz and 0.9 V s^{-1} respectively. Voltammetric response was linear in 3 ranges, 70–110 μM , 20–60 μM and 2–10 μM with regression coefficient of 0.9873, 0.9978 and 0.9935 respectively and limit of detection 0.47 μM for total water soluble phthalates in aqueous medium. The developed method was successfully applied for total phthalates determination in various samples of water stored in PVC coolers and plastic bottles.

PP-45

AN IDEA FOR ION-SELECTIVE SENSOR: MODIFICATION OF THE GOLD ELECTRODE SURFACE BY CALIX[4]ARENE SELF-ASSEMBLED MONOLAYER

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The aim of this work is the use of molecules which belong in the large group of substances permitting transport of ions through biochemical membranes (ionophores) for development of an electrochemical, ion-selective sensor.

The modified, synthesized calixarene molecules, with four sulphur-containing groups located at the lower rim, were used as the ionophores. The calixarene molecules were covalently bonded to the surface of a gold disk electrode through the sulphur atoms. A self-assembled monolayer (SAM) was formed on the electrode surface, which altered the electro-

chemical properties of the electrode, compared to the bare electrode.

The preliminary results, obtained by the atomic force microscopy (AFM) measurements, indicate that the calixarene molecules form aggregates on the electrode surface, which have monodisperse size, and the calixarene SAM inhibits the gold electrode oxidation.

Electrochemical measurements by cyclic voltammetry permitted the calculation of a Langmuir-type adsorption isotherm for the formation of the calixarene SAM. Two modes of the calixarene adsorption process were compared, adsorption in the absence of any external electric potential applied to the gold electrode, and the electrochemical adsorption. It seems that calixarenes are more readily adsorbed from chloroform solutions, without applying any potential to the electrode. Electrochemical impedance spectroscopic measurements have demonstrated that the SAM-covered electrode has the impedance different from that of the bare electrode.

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PP-46

EVLS AS A NOVEL AND PROMISING MATHEMATICAL APPROACH IN VOLTAMMETRIC METHODS

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Cyclic Voltammetry (CV) and Square Wave Voltammetry (SWV) belong to the most powerful electrochemical techniques that can be applied for both analytical and electrokinetic measurements at static drop or solid electrodes¹, because these methods, on one hand, are easy-to-use and low cost with fast scan rates and, on the other hand, have the ability to show the reversibility of redox reactions². In addition, Elimination Voltammetry with Linear Scan (EVLS) belongs to the newest powerful electrochemical tools. This method provides an improvement of voltammetric results through eliminating and conserving various particular currents, of which the total recorded current is composed³⁻⁵. The elimination process provides further information on electrochemical

mechanisms. In this study, the behavior of Cd(II), Zn(II) and Cu(II) in the presence of chloride ions (pH ranging from 3 to 9) at two electrodes, particularly, paraffin impregnated graphite electrode (PIGE) and hanging mercury drop electrode (HMDE), measured by CV and SWV was compared. The voltammetric data was further processed by EVLS. The values of elimination coefficients of elimination functions for different scan rate combinations were calculated by Matlab program.

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PP-47

THE DETERMINATION OF DIZEPAM, TEMAZEPAM AND OXAZEPAM AT THE LEAD FILM ELECTRODE BY ADSORPTIVE STRIPPING VOLTAMMETRY

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The determination of psychoactive 1,4-benzodiazepine drugs is of relevant interest in clinical, biomedical areas. The voltammetry methods seem to be efficient tools for a quantitative determination of 1,4-benzodiazepine drugs in pharmaceutical preparations and biological fluids in a simple and economic way. Therefore highly sensitive and simple voltammetric method for the determination of temazepam, diazepam and oxazepam at *in situ* plated lead film electrode was developed.

Till now the lead film electrode has been used for the determination of inorganic ions¹ such as Ni(II), Co(II), U(VI), Mo(VI) and organic compounds² such as folic acid, trimethoprim, testosterone, glipizide, rifampicine, rutin and sildenafil citrate (Viagra). Although lead compounds used for plating a lead film are toxic, their toxicity and volatility is

lower as compared to the mercury and mercury compounds used for the preparation of mercury electrodes.

In this presentation it was shown that determination of 1,4-benzodiazepine drugs by adsorptive stripping voltammetry was possible using an *in situ* plated lead film electrode. The proposed procedures are based on temazepam, diazepam and oxazepam adsorption on the lead film electrode in the accumulation step and then the reduction of compounds during the stripping step.

The optimized procedures were applied to the determination of temazepam and diazepam in the presence of other components in pharmaceutical preparations with minimum sample manipulation. The analysis of diazepam and temazepam were performed much more rapidly than by previously reported voltammetric techniques. The procedure for determination of oxazepam was successfully used for determination of this compound in human urine samples directly without any separation steps.

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PP-48

ON LINE DIFFERENTIAL PULSE POLAROGRAPHIC DETERMINATION OF COBALT(II) AT PPB CONCENTRATIONS IN ZN PLANT ELECTROLYTE

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The purification process control of industrial ZnSO₄ solutions used for Zn electroextraction requires simple, rapid and reliable methods for trace (ppb) concentrations determination of: Cd²⁺, Cu²⁺, Pb²⁺, Sb³⁺, Co²⁺, Ni²⁺, Ge⁴⁺ in the presence of about 150 g L⁻¹ ZnSO₄. The high Zn²⁺ concentration makes the application of the AAS and ICP complicated, long and less precise, requiring preliminary laboratory analyte separation.

The high ionic concentrations of the Zn plant electrolyte however favors the application of the voltammetric methods for the determination of almost all these impurities except Co²⁺ and Ni²⁺ defined by Bond as impossible¹ because of the complete peak overlapping with the huge peak of Zn²⁺.

A simple and rapid Differential Pulse Polarographic (DPP) method with DME application for direct on line Co²⁺ determination in Zn plant electrolyte was developed and tested with real industrial solutions. The method is based on the Co²⁺ to Co³⁺ oxidation by 1-nitrozo-2-naphtol in pH 9 ammonia buffer used as supporting electrolyte in which the sample is added directly on line. The DPP Co³⁺ peak appear at

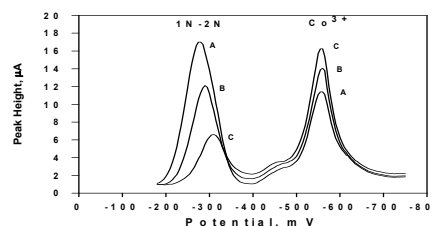


Fig. 1. DPP curves of ammonia buffer with pH 9, containing 1-nitrozo-2-naphtol and Co²⁺ additions of: 4 ppb (curve A), 5 ppb (curve B) and 6 ppb (Curve C). $\Delta E = -50$ mV

-550 mV (SCE) and the great $E_{1/2}$ potential difference completely eliminates the Zn²⁺ interference as shown in Fig. 1.

Unlike the stripping method of Brainina² based on electrochemical deposition of 1-nitrozo-2-naphtol chelate of Co³⁺ layer on a graphite electrode followed by DC anodic dissolution, the proposed DPP determination is direct and rapid. The high precision of the results (4.2 % rel. at 20 ppb) and the wide linear concentration range covering entire range of Co²⁺ concentrations in Zn plant electrolyte (from 1 to about 500 ppb) make it suitable for on-line application.

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PP-49

IN SITU As(III) DETERMINATION IN THE PRESENCE OF Pb(II) BY DIFFERENTIAL ALTERNATIVE PULSES VOLTAMMETRY

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The Differential Alternative Pulses Voltammetry (DAPV) introduced by the author earlier¹ combines the high sensitivity of the Differential Pulse Polarography (DPP) and the high resolution power of the second order polarographic techniques. The small peaks half-width and the shape of the DAPV curve, as second derivative of the polarographic wave allow direct simultaneous determination of species having very small $E_{1/2}$ difference as well as at high concentration ratios using the peaks situated at both side of the zero line (Figure 1).

DAPV was applied for direct determination of As(III) in ground water containing also Pb(II) using HCl as supporting electrolyte where the As(III)/Pb(II) $E_{1/2}$ difference is about 40 mV. No chemical pretreatment procedure was applied for analyte separation. Complete peak overlapping occurs at 0.5:1 Pb(II) to As(III) concentration ratio applying DPP, while the DAPV application yields distinct peaks registration up to ratio as high as 12:1. The DAPV allows reliable, rapid, simple and

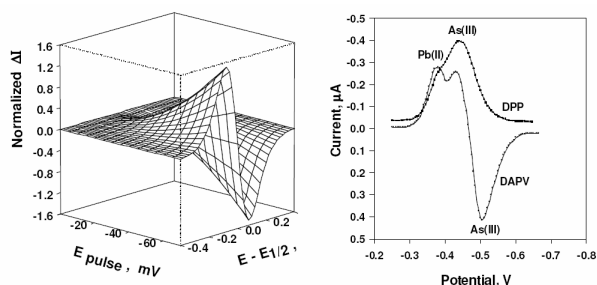


Fig. 1. Theoretical DAPV curves (left); DPP and DAPV polarograms of Pb(II) and As(III) at 0.5:1 ratio in HCl (right)

precise *in situ* As(III) determination preventing thus its oxidation to electrochemically inactive As(V) by the oxygen during the sample transportation to the analytical laboratory.

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PP-50

THE USE OF MERCURY MENISCUS MODIFIED SILVER SOLID AMALGAM ELECTRODE IN VOLTAMMETRIC ANALYSIS OF GENOTOXIC NITRO DERIVATIVES OF FLUORENE AND 9-FLUORENONE

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Nitro derivatives of polycyclic aromatic hydrocarbons (NPAHs) originate mainly from anthropogenic fossil fuel combustion and belong to the group of genotoxic compounds with proven negative biological effect on living organisms. That is why the need for extremely sensitive and selective methods of NPAHs determination is still growing¹. Easy electrochemical reducibility of nitro group at aromatic rings enables successful use of electroanalytical methods for NPAHs determination². Recently, great attention has been paid to electrochemical determination of nitro derivatives of fluorene and 9-fluorenone (namely 2-nitrofluorene, 2,7-dinitro-

fluorene, 2-nitro-9-fluorenone and 2,7-dinitro-9-fluorenone) at a hanging mercury drop electrode (HMDE) (ref.²). In this work, the main disadvantage of HMDE – low mechanical stability of mercury drop limiting the use of this electrode for field applications – has been eliminated by using the mechanically robust mercury meniscus modified silver solid amalgam electrode (m-AgSAE) (ref.³).

DC voltammetry (DCV) and differential pulse voltammetry (DPV) at m-AgSAE have been used for the determination of genotoxic fluorene derivatives mentioned above. Reached limits of quantification were around 10⁻⁶ M for DCV at m-AgSAE and M for DPV at m-AgSAE. Obtained results were compared with previous determinations of these substances at mercury electrodes². The electrode mechanisms of tested substances at m-AgSAE have been also proposed and discussed.

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PP-51

EFFECT OF POLY(DIMETHYLDIALLYLAMMONIUM CHLORIDE) ON ENZYME ENCAPSULATION INTO A SOL-GEL MATRIX

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Modification of sol-gel materials for development of organic-inorganic hybrid materials with additional properties or improved performance is a fast growing field for surface treatment technology¹, and (bio)sensing applications². One convenient route to form a hybrid is the introduction of a polymer into the sol-gel matrix. This macromolecular compound can provide additional reactivity depending on the chemical functions hold by the polymer while the inorganic matrix induces good mechanical stability and suitable porosity. This kind of composite has been successfully used for electroanalysis when doped with poly(vinylsulfonic acid) or poly(dimethyldiallylammonium chloride) (PDMDAAC) (ref.³). The ion-exchange properties of the encapsulated polyelectrolyte allow using this sensor, for example, in Hanford tank waste simulant solution⁴.

Silica sol-gel is considered as a favourable matrix for long time encapsulation of protein or even whole cells⁵. We are currently interested in the encapsulation of D-Sorbitol Dehydrogenase and Galactitol Dehydrogenase for applications in electroenzymatic synthesis. We observed that the direct encapsulation into a pure silica sol-gel matrix led to total suppression of enzyme activity, as characterized electrochemically. The lack of diffusion into the gel or the unfavourable electrostatic environment created by surface silanol groups could explain this inactivity. We will show here that the introduction of the suitable content of PDMDAAC into the sol during the bioencapsulation permits to maintain very good catalytic properties. This polyelectrolyte, in combination with sol-gel allows the elaboration of stable modified electrode. This is an important step for the development of electrochemical reactors based on immobilized enzymes.

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PRUSSIAN BLUE BASED PLANAR BIOSENSOR FOR LACTATE DETERMINATION IN BLOOD AND SWEAT

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The construction of sensors is based on the approach for operation of oxidase based biosensors on electrodes modified by electrochemically deposited Prussian Blue (ferric hexacyanoferrate). The approach was first demonstrated by our team in 1994 (ref.¹) and had been developed in order to achieve the most advantageous H₂O₂ transducer.

Electrochemical biosensor for lactate has been made by immobilization of the enzyme lactate oxidase on the top of planar sensor for hydrogen peroxide produced by Ltd Rusens. Immobilization protocol included a formation of the enzyme containing R-oxy siloxane membrane according to procedure developed earlier². Exposure of lactate oxidase to water-organic mixtures with a high (90 %) content of the organic

solvent, resulted in stabilization of the enzyme by membrane-forming polyelectrolyte. The corresponding biosensor has following analytical characteristics: improved sensitivity (about 70 mA M⁻¹ cm⁻²) and signal-to-noise ratio, low detection limit to compare with known analogs. Lactate may be analyzed in range from 1×10⁻⁶ M to 1×10⁻³ M in FIA regime.

During intensive sport training the concentration of lactate increases in 10–15 times in comparison with basic concentration. The dynamics of lactate concentration increasing allows to determine the most perspective athlete in such activities as boat racing, athletics, cross country skiing. The task was to develop the non-invasive methods of lactate determination. The most suitable biological liquid for such determination is sweat. In this research we used developed biosensors for determination lactate in blood and sweat as well as for estimation their correlation during sports training.

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PP-53

DETERMINATION OF 1-NITROPYRENE, 1-HYDROXYPYRENE AND 1-AMINOPYRENE IN HUMAN URINE BY HPLC WITH ELECTROCHEMICAL DETECTION BASED ON BORON DOPED DIAMOND FILM ELECTRODE

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Many polycyclic aromatic hydrocarbons (PAHs) and nitrated polycyclic aromatic hydrocarbons (NPAHs) are well known to be carcinogenic or co-carcinogenic compounds¹. For example, 1-nitropyrene is one of the most abundant representatives of nitro aromatic compounds in the environment which has also been detected in automobile exhaust gas, urban air, exhalation from the incinerators, and in certain food-stuffs such as grilled meats or teas²⁻⁴. It is also listed in the IARC Monographs on the Evaluation of Carcinogenic Risks to Humans in the group 2B (possibly carcinogenic to humans).

A valuable tool in assessing human exposure to PAHs and NPAHs is the use of biological markers. 1-Nitropyrene (1-NP) and its urinary metabolites 1-aminopyrene (1-AP) and 1-hydroxypyrene (1-HP) have been proposed as biological markers for these purposes.

Most of analyses of PAHs and NPAHs in environmental samples are carried out by gas chromatography coupled with mass spectrometry, or by high performance liquid chromatog-

raphy (HPLC) with fluorescence detector or UV/VIS detector. However, these methods are characterized by high investment and running costs. Because these analytes are easy electrochemically oxidizable and/or reducible, we have investigated the possibility of their determination by HPLC coupled with electrochemical detection based on boron doped diamond film electrode. We have found that this type of detection is sufficiently sensitive, selective and moreover it has much lower investment and running costs.

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PP-54

ENRICHMENT OF HYDRIODIC ACID USING ELECTRODIALYSIS CELL IN SULFUR IODINE PROCESS FOR HYDROGEN PRODUCTION

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The present work investigates the electro dialysis cell for concentrating hydriodic acid in thermochemical water-splitting sulfur iodine (SI) process for hydrogen production. The SI process consists of three coupled chemical reactions, such as the Bunsen reaction, the sulphuric acid decomposition reaction, and the HI decomposition reaction¹. The hydriodic acid concentration part in HI decomposition section is the most energy consuming process because the HI_x solution (HI–I₂–H₂O mixture) produced from the Bunsen reaction is present as an azeotropic mixture². Therefore, the distillation part to concentrate the hydriodic acid requires considerable excess thermal energy, which can decrease the overall thermal efficiency of the SI process. Our research group reported that overall thermal efficiency is crucially influenced by both cell voltage and water transport of the electro dialysis cell³. In this work, the electro dialysis cell were prepared by consisting a polymer electrolyte membrane sandwiched between two carbon electrodes, gaskets, and carbon blocks with flow channels for distributing the reactant HI_x solution⁴. The cell voltage and water transport were measured with different operating conditions and their results were analyzed by combining theoretical calculations.

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PP-55

AN INVESTIGATION OF THE ELECTRO-CATALYST USED AS ELECTRODE MATERIALS IN SO₂-DEPOLARIZED ELECTROLYZER

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The SO₂-depolarized electrolyzer (SDE) used in the hybrid sulfur process oxidizes sulfur dioxide to form sulfuric acid at the anode¹ and reduces protons to form hydrogen at the cathode². The important attribute of the SDE is the lowering of the electrode potential for producing hydrogen from 1.23 V vs. reversible hydrogen electrode (RHE), which is the equilibrium potential at standard state pure water electrolysis, to 0.158 V_{RHE} (ref.³). This means that SDE could more efficiently produce hydrogen with lower power as compared with pure water electrolysis. It was reported that 390 mV_{RHE} overpotential were generated at the anode and 50 mV_{RHE} at the cathode in the SDE, when 200 mA cm⁻² of current density was applied during SO₂ oxidation reaction in a 50 wt.% H₂SO₄ solution. Therefore, it is necessary to reduce the anodic overpotential in order to improve the performance of the SDE. In the present work, the electro-catalyst utilization at anode was estimated using cyclic voltammograms (CVs) as a function of catalyst loading amount in a deaerated 4.8 wt.% H₂SO₄ solution. Then the CVs were measured on the electro-catalyst in SO₂-free and SO₂-saturated 50 wt.% H₂SO₄ solutions in order to confirm the mechanism of SO₂ oxidation reaction. Finally, linear sweep voltammograms were obtained with various loading amounts in order to determine the effect of loading amount on SO₂ oxidation reaction.

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PP-56**ELECTROCHEMICAL REMEDIATION. PAIRED RECOVERY OF A SOIL METAL POLLUTANT AND ITS EXTRACTANT, AT THE MICROSCALE LEVEL**

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Soil are frequently the depositories of a wide range of wastes^{1,2}, atmospheric deposition can also contribute to soil pollution. Prevention strategies can undoubtedly ameliorate this problem; however, remediation technologies are of immediate emergency in many instances.

There is a wide variety of soil remediation based on physical, chemical, electrochemical or biochemical principles^{3,5}. A modern alternative is metal complexation. It is based on the idea that metal complexes with chelating agents are frequently soluble and generally quite strong due to the chelate effect. Is it that, polluting metal ions is difficult to

remove from chelate containing washing solutions by alkalization, due to the intrinsic thermodynamic stabilities of the metal chelates.

The objective of this work was development an experiment in microscale to demonstrate the removal of a metal from an insoluble compound of $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ and EDTA by complexation followed by the simultaneous electrochemical recovery of the ligand (EDTA) and the metal (Cu) in its elemental form.

To recover both, the polluting metal and the extractant, an electrochemical process is worn. Using a micro electrochemical cell with a small U-tube, that containing the Cu-EDTA solution, and introduced a Pt wire into one arm of the tube as anode, and a graphite rod in the other arm as the cathode, at an applied potential of 10–11 V.

In this treatment, metal is recovered (in its elemental form), as well as the chelating agent (in its tetraprotonated form). Both products are evident by visual inspection.

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