YISAC 2017

24th Young Investigators Seminar on Analytical Chemistry

Venice, June 28th - 30th 2017

Book of Abstracts

Building DELTA

Room 0A

Scientific Campus, Via Torino 155, Mestre
Venice, Italy

Scientific committe

University of Graz, Austria
Kurt Kalcher, kurt.kalcher@uni-graz.at
Kevin Francesconi, kevin.francesconi@uni-graz.at
Walter Goessler, walter.goessler@uni-graz.at

Graz University of Technology, Austria
Ernst Lankmayr, lankmayr@tugraz.at

University of Pardubice, Czech Republic
Radovan Metelka, radovan.metelka@upce.cz
Karel Vytřas, karel.vytras@upce.cz

University of Szeged, Hungary
Zoltán Kónya, konya@chem.u-szeged.hu

University of Venice, Italy
Ligia Maria Moretto, moretto@unive.it
Paolo Ugo, ugo@unive.it

AGH University of Science and Technology, Kraków, Poland
Andrzej Bobrowski, gcbobrow@cyf-kr.edu.pl

University of Lodz, Poland
Sławomira Skrzypek, skrzypek@uni.lodz.pl

University of Novi Sad, Serbia
Biljana Abramović, biljana.abramovic@dh.uns.ac.rs
Božo Dalmacija, bozo.dalmacija@dh.uns.ac.rs
Valéria Guzsvány, valeria.guzsvany@dh.uns.ac.rs
Sanja Lazić, sanjal@polj.uns.ac.rs
Srđan Rončević, srdjan.roncevic@dh.uns.ac.rs

University of Ljubljana, Slovenia
Helena Prosen, helena.prosen@fkkt.uni-lj.si
Polonca Trebše, polonca.trebse@zf.uni-lj.si
Marjan Veber, marjan.veber@fkkt.uni-lj.si

Institute Jožef Stefan, Ljubljana, Slovenia
Vekoslava Stibilj, vekoslava.stibilj@ijs.si

National Institute of Chemistry, Ljubljana, Slovenia
Samo Hočevar, samo.hocevar@ki.si
Mitja Kolar, mitja.kolar@fkkt.uni-lj.si
Božidar Ogorevc, bozidar.ogorevc@ki.si

University of Nova Gorica, Slovenia
Mladen Franko, mladen.franko@ung.si

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Program

Building DELTA

Room 0A

June 28th, 2017

17:00–19:00 **Registration and Get-together party -** Building ALFA -1

June 29th, 2017

Morning

08:30-09:00 **Registration**

09:00-09:30 **Opening YISAC 2017**

09:30-10:45 *Session I* **- Sensors - chair: Maria Sole Zalaffi**

09:30-09:45	Krulišová Pavla	Electrochemical immunosensor based on antibody-nanoparticle conjugates as a potential tool for rapid detection of foodborne pathogenes
09:45-10:00	Possan André	Gold Surfaces Evaluation for Improvement in Magnetoelastic Biosensors
10:00-10:15	Kovařová Aneta	Quantum dots-modified silica nanoparticles as immunosensing platform allowing simultaneous electrochemical detection of cancer biomarkers
10:15-10:30	Kaczmarska Kinga	Modification of edge plane pyrolytic graphite electrode with graphene nanoplatelets for fabrication of highly sensitive electrochemical sensor
10:30-10:45	Kašparová Jitka	Dendrimers as a key component of detection probes in various bioapplications

10:45–11:15 Coffee break

11:15-13:00 *Session II* **- Chromatography I - chair: Ida Kraševec**

11:15-11:30	Piechocka Justyna	High performance liquid chromatography of endogenic thiols and aldehydes
11:30-11:45	Kroepfl Nina	Quantitative determination of ergothioneine by HPLC/ICP-QQQ-MS
11:45-12:00	Ocvirk Miha	Dynamic of isomerization of Hop (Humulus lupulus L) alpha-acids in brewing process
12:00-12:15	Glabonjat Ronald	A novel arsenolipid biosynthesised by Dunaliella tertiolecta under controlled culturing conditions
12:15-12:30	Mohorič Urška	Hyphenation of surfactant-free microemulsion electrokinetic chromatography (SF-MEEKC) with ESI-MS and UV detection for the determination of water- and fat-soluble neutral vitamins
12:30–12:45	Surmová Silvie	Application of different extraction methods to characterize the Tonka bean extract volatile profile
12:45-13:00	Kučerová Simona	Natural antimicrobial substances and their use it the food industry

13:00–14:15 Lunch

Afternoon

14:15-15:45 *Session III* **- Electroanalysis I - chair: Pavlina Martinkova**

14:15-14:30	Węgiel Krystian	Voltammetric behaviour of mandelic acid–titanium(IV)–chlorate(V) system at the bismuth bulk electrode
14:30-14:45	Śliwa Julia	Application of Novel Tellurium Film Electrode for Copper(II) Determination by Means of Anodic Stripping Voltammetry
14:45-15:00	Robak Justyna	The voltammetric determination of antioxidant – syringic acid
15:00-15:15	Žabčíková Simona	Optimization of retinol extraction into the carbon paste electrode from milk samples
15:15-15:30	Rudnicki Konrad	Electrochemical study of the ionophoric antibiotic – monensin and its voltammetric determination in a forage for horses
15:30-15:45	Gričar Ema	Electrochemical study of interactions between phytates and selected metal ions

16:00-16:30 Coffee break

16:30-18:00 *Session IV* - **Chromatography II - chair: Glabonjat Ronald**

16:30-16:45	Ivanović Milena	Deep Eutectic Solvents (DES): Green extraction of phenolic compounds from chokeberries (Aronia melanocarpa)
16:45-17:00	Topic Jelena	The comparison of anthocyanin and pyranoanthocyanin extraction efficiency in Pinot Noir wine using SPE
17:00-17:15	Adámková Karolína	Determination of bitter acids for the various species of hops and comparing their contents in beer prepared by so called dry hopping
17:15-17:30	Mrzlikar Miha	Analysis of Neonicotinoid Pesticides in Honey
17:30-17:45	Stiboller Michael	Distribution of arsenic and its species in human milk
17:45-18:00	Rizzato Giovanni	Metabolomics for characterizations of officinal herbs: the case of Helichrysum species

19:00-22:00 Social dinner

June 30th, 2017

Morning

09:00-10:45 *Session V* **- Chromatography III - chair: Kroepfl Nina**

09:00-09:15	Tasić Ana	Investigation of thiacloprid removal from water media by magnetite modified multiwalled carbon nanotubes
09:15-09:30	Callegaro Alice	Multi-biomarker analysis of sediments for paleoclimate research
09:30-09:45	Kraševec Ida	Development of a hollow fibre microextraction method for determination of benzotriazoles
09:45-10:00	Padoan Sara	Determination of ionic compounds in Antarctic samples using ion-chromatography coupled to mass spectrometry
10:00-10:15	Zanutto P. C. Clariana	Production and characterization of whey peptides bioactive in a packed bed reactor (PBR)
10:15-10:30	Zupančič Urška	The influence of selected oxide pigments on drying of linseed oil

10:30-11:00 Coffee break

11:00-13:00 *Session VI* **- Electronalysis II - chair: Śliwa Julia**

11:00-11:15	Vajdle Olga	Voltammetric determination of macrolide antibiotic azithromycin in the pharmaceutical preparation by carbon paste electrode surface modified with gold nanoparticles
11:15-11:30	Štěpánková Michaela	Comparison Study of Voltammetric Determination of Mesalazine Using Boron-doped Diamond Electrodes with Different Content of Boron
11:30-11:45	Sipa Karolina	Preparation, characterization, and electrochemical application of ultra-trace graphite electrode modified with namomaterials
11:45-12:00	Martinková Pavlína	Surface and electrochemical characterization of boron-doped diamond electrodes with different content of boron
12:00-12:15	Festinger Natalia	Properties of screen printed gold electrodes modified with carbon nanomaterials

12:30-13:45 Lunch

Afternoon

13:45-15:15 *Session VII* **- Spectroscopy and polymers - chair: Padoan Sara**

13:45-14:00	Goljat Leja	Comparison of Colorimetric Reagents and Their Applicability in Thermal-Lens Spectrometry
14:00-14:15	Bednářová Kristýna	Development of the ICP-OES method for determining iodine
14:15-14:30	Petronijevic Mirjana	The Allium test - a tool for monitoring the potential health risk of utilizing H_2O_2/UV advanced oxidation processes in drinking water treatment
14:30-14:45	Czarny Karolina	The influence of hormones on water organism and the methods for their determination
14:45-15:00	Mavrič Andraž	Efficient de-agglomeration of polysilane macromolecules in solution and their molecular size
15:00-15:15	Golub Doris	Functionalized high surface area vinylbenzyl chloride polyHIPES

15:30-16:00 Coffee break

16:00-17:00 *Session VIII* **- Electroanalysis III - chair: Natalia Festinger**

16:00-16:15	Azevedo Beluomini Maísa	Development of an electrochemical sensor based on electropolymerized molecularly imprinted polymer on modified gold nanowire electrodes for L-arabitol detection in sugarcane vinasse.
16:15-16:30	Kołodziejczyk Karina	The effects of constant magnetic field on metal electrodeposition
16:30-16:45	Ceolotto Nicola	Preparation and characterization of nanoelectrodes ensembles and disks microelectrodes
16:45-17:00	Zalaffi Maria Sole	Advanced nanomaterials and nanoparticles for electrochemical and SERS applications

17:00-17:30 Closing ceremony

Abstracts

Electrochemical immunosensor based on antibody-nanoparticle conjugates as a potential tool for rapid detection of foodborne pathogens.

Pavla Krulisova, Aneta Kovarova, Lucie Korecka and Zuzana Bilkova

Department of Biological and Biochemical Sciences, Faculty of Chemical Technology, University of Pardubice, Studentska 573, 532 10 Pardubice, Czech Republic

Food borne illnesses caused by pathogens and their toxins pose serious threat for human health. There are many pathogens identified as cause of food-borne outbreaks but for the most of them are responsible especially *Salmonella spp., Listeria monocytogenes* and *Escherichia coli*[1, 2]. The conventional methods for their detection comprise of pathogens pre-enrichment, selective enrichment and selective plating followed by standard biochemical identifications, methods of molecular biology as well as serological confirmation. While these conventional methods are generally regarded as a "golden standard", they are considerably limited by assay time which can be up to one week[3]. Therefore, development of more efficient and faster method allowing direct detection and identification of food-borne pathogen bacteria is now of great importance worldwide.

One of very promising tools seems to be electrochemical immunosensor generally based on reaction of detected bacteria and two specific antibodies. One serves, in combination with magnetic particles, for efficient capture of determined bacteria even from the complex sample. Second antibody is responsible for generation of final detection signal originated from sensitive probe linked to the antibody molecule. In this study, we have focused on the use of new types of probes, concretely gold nanoparticles and quantum dots. Square wave stripping voltammetry was used as detection method. Due to its simplicity and timelessness this type of biosensor, especially in combination with miniaturized disposable screen-printed electrodes, which are used for analysis, should be promising for use in quickly screening bacterial contamination in food[4].

Acknowledgement
This work was supported by the European Union´s LOVE-FOOD 2 MARKET project under the contract No. 687681.

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Gold Surfaces Evaluation for Improvement in Magnetoelastic Biosensors

André L. Possan[1], Frank P. Missell[1] and Ligia M. Moretto[2]

[1] *Centro de Ciências Exatas e Tecnologias, Universidade de Caxias do Sul, Caxias do Sul, RS, Brasil.*
[2] *Department of Molecular Sciences and Nanosystems, University Ca' Foscari of Venice, Via Torino, 155, 30170 Mestre,Venice, Italy.*

The problems connected with the strong presence of bacteria such as Escherichia coli and viruses as Zika, in the environment and food industries in several countries, made the governments encourage the academic community to improve easy and sensitive detection systems for these species. In recent years, a great interest has focused on surface-based affinity biosensors, exploiting several transduction methods to monitor the binding reactions at the interface sensor-solution. Mass sensitive magnetoelastic sensors constitute a very attractive, versatile and useful platform for monitoring antibody-antigen reaction exploiting the mass change of this linking[1]. In our project of developing an immuno-magnetoelastic sensor, the immobilization of the system antibody-antigen on the strip surface is based on its bounding through a thiol monolayer formed on a gold thin film deposited on the magnetoelastic strip. In this work, we present the study and optimization of the gold layer deposited, in order to obtain the best performance of the sensor. According to the literature, the deposition of antigen-antibody systems is improved on the surface with lower roughness[2,3,4]. To this aim, two different techniques of gold deposition on the strips of amorphous Metglas 2826MB3 are tested, that are sputtering of chromium-gold layers and direct electroplating of gold. The gold surfaces were analysed by profilometry 2D (µm level), AFM (nm level), microscopy and Rutherford backscattering spectroscopy (RBS). The results obtained have shown that the electroplated Au, with a thickness in the order of 104 nm, does not suffer of a delamination process, while this phenomenon was observed in the sputtered chromium-gold layers. The comparison of the roughness showed that the Au electroplating surface presents lower values, suggesting that the choice of this procedure can improve the efficiency of the immunosensor.

Acknowledgement
This work was supported by Capes PDSE doctoral program (88881.135894/2016-01).

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Quantum dots-modified silica nanoparticles as immunosensing platform allowing simultaneous electrochemical detection of cancer biomarkers

Aneta Kovarova[1], Jana Drbohlavova[2], Zuzana Bilkova[1] and Lucie Korecka[1]

[1] *Department of Biological and Biochemical Sciences, Faculty of Chemical Technology, University of Pardubice, Studentska 573, 532 10 Pardubice, Czech Republic*
[2] *Central European Institute of Technology, Brno University of Technology, Purkynova 123, 616 00 Brno, Czech Republic*

Nowadays, there is an effort to determine simultaneously two or more biomarkers within one analysis allowing to improve selectivity in diagnosis of the disease. Quantum dots (QDs), semiconductor nanoparticles composed of various heavy metals, could be advantageously used as labels of antibodies in QDs-linked immunosorbent assays (QLISA)[1,2]. Electrochemical detection of QDs, based on monitoring of current response of metal ions released from QDs after dissolution in acetic medium, provide us the possibility of multiple biomarkers analysis[3]. Moreover, mesoporous silica nanoparticles (SiNPs) are useful in bioanalyses for their large surface area. These features of SiNPs enable to bind higher amounts of QDs to $SiNP_S$ and therefore to antibodies leading to increased current response[4]. Specific antibodies allowing detection of protein biomarkers of ovarian cancer, α-fetoprotein (AFP) and epididymal protein 4 (HE4), were prepared and used for construction of sensitive magneto-immunosensor of arrangement described on Fig. 1. Square wave anodic stripping voltammetry (SWASV) was used as a detection technique and measurements were realised on bismuth film modified carbon screen printed electrodes (BiSPCE).

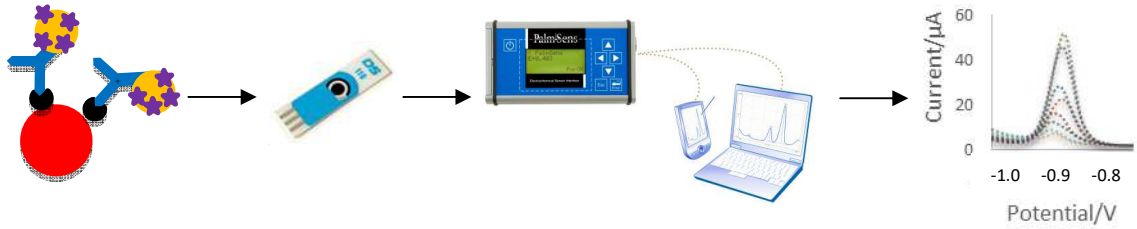

Fig. 1. Arrangement of magneto-immunosensor for simultaneous electrochemical detection of antigens AFP and HE4 by use of antibodies labelled by QDs-modified silica nanoparticles

Acknowledgement
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Modification of edge plane pyrolytic graphite electrode with graphene nanoplatelets for fabrication of highly sensitive electrochemical sensor

Kinga Kaczmarska, Mariola Brycht, Andrzej Leniart, Sławomira Skrzypek and Karolina Sipa

University of Lodz, Faculty of Chemistry, Department of Inorganic and Analytical Chemistry, Tamka Str. 12, 91-403 Łódź, Poland

Edge plane pyrolytic graphite electrode (EPPGE) is a relatively new, environmentally friendly, and perspective carbon-based electrode material. The EPPGE is used in voltammetry as working electrode on the grounds of low background current, long term stability and reproducibility, high selectivity and sensitivity. Moreover, EPPGE is characterized by strong adsorption properties and wide electrochemical window in aqueous solutions.

Graphene nanoplatelets (GNP) are carbon nanostructure made up of graphene sheets with a total thickness of one to several tens of nanometers. The GNP production is simpler and less expensive compared to other nanostructures such as carbon nanotubes (CNTs). The use of GNP for modification of solid electrodes can improve their electrochemical properties of electrode.

Oxolinic acid (*OxA*) is a synthetic, veterinary and quinolone antibiotic. *OxA* affects the replication of the nucleic acid molecule in bacteria. OxA is dedicated for use in infections of genitourinary system.

In the present work, the possibilities of edge plane pyrolytic graphite electrode modified with graphene nanoplatelets for the determination of *OxA* by square wave voltammetry (SWV) are presented. The experimental conditions, *i.e.* pH of the supporting electrolyte, an amplitude, a frequency, and a step potential, were optimized. A rapid, simple, selective and sensitive SWV procedure to determine *OxA* was performed in the concentration range of 3.0×10^{-7} –9.1×10^{-6} mol L^{-1}. Furthermore, a biological relevance of the developed SWV procedure was demonstrated by quantitative analysis of the spiked human urine samples. The influence of some interfering compounds and ions was also evaluated. To understand the electrochemical oxidation mechanism of *OxA* on GNP/EPPGE, the cyclic voltammetry (CV) was employed. Moreover, the surface topography and morphology of the GNP/EPPGE was characterized by atomic force microscopy (AFM).

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Dendrimers as a key component of detection probes in various bioapplications

Jitka Kasparova[1], Aneta Kovarova[1], Jiri Palarcik[2], Lenka Ceslova[3], Zuzana Bilkova[1] and Lucie Korecka[1]

[1] *Department of Biological and Biochemical Sciences*
[2] *Institute of Environmental and Chemical Engineering*
[3] *Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentska 573, 532 10 Pardubice, Czech Republic.*

Hyperbranched polymeric 3D structures are known as dendrimers which name reflecting its structure reminding crown tree and its branches. This structure typically contains central molecule forming core. Crown of the dendrimers is formed by cascade branching outwards from the core. Exactly defined amount of amino, carboxyl, hydroxyl or other functional groups, usually located on the top of the dendrimers, allowing attachment of high amounts of various molecules (enzymes, drugs, antibodies, etc.) to gain highly biofunctionalized carriers for further applications[1,2].

Due to functionalization of dendrimers raise its usefulness thanks to good water solubility and biocompatibility, up to now dendrimers have been used in many biomedical applications in immunology, drug delivery, tissue engineering, gene therapy/delivery or as well as catalysts in industry, pigments or optoelectronics. Dendrimers found applicability also in luminescence detection or electrochemical biosensors[1,3-5].

Our work deals with incorporation of fluorescence tags to polyamidoamine (PAMAM) dendrimers. Prepared probes are suitable for fluorescence detection or detection by electrochemical biosensors.

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High performance liquid chromatography of endogenic thiols and aldehydes

Justyna Piechocka, Monika Wyszczelska-Rokiel and Rafał Głowacki

University of Łódź, Faculty of Chemistry, Department of Environmental Chemistry, Pomorska 163 Str., 90-236 Łódź (Poland)

Civilization diseases, such as cancers and cardiovascular diseases, are the most frequent reasons of mortality of humans in industrialized countries. Accumulating evidences indicate that plasma homocysteine (Hcy) and metabolically related compounds are associated with these disorders and can act as strong predictors of mortality. It has been also demonstrated that, daily supplementary treatments with vitamin B (including B6) have a beneficial role in reducing the risk of coronary heart disease, nonfatal myocardial infarction and hypertension[1]. Unfortunately, the reason(s) for the beneficial impact of vitamin B6 are still unclear.

The B vitamins are a group of water soluble, chemically quite distinct compounds involved in a variety of important functions, to which vitamin B6 also belongs. According to literature data, pyridoxal 5`-phosphate (PLP) that is the biologically most active form of vitamin B6 is an enzymatic co-factor required for more than 140 biochemical reactions including sugar and fatty acid metabolism as well as amino acid biosynthesis and degradation. Particularly, it acts as an essential coenzyme for cystathionine *β*-synthase and cystathionine *γ*-lyase that participate in the transsulfuration of Hcy to cysteine (Cys)[2]. PLP is also known to undergo facile condensation reaction with Cys and Hcy affording 2-pyridoxyl-1,3-thiazolidine-4-carboxylic acid (Cys-PLP)[3] and 2-pyridoxyl-1,4-thiazine-4-carboxylic acid (Hcy-PLP)[4-6], respectively.

In recent years, we have demonstrated that Cys and Hcy react with PLP under physiological conditions in phosphate buffer[6]. Due to the fact that Hcy, Cys and PLP are ubiquitous in biological fluids, we have concluded that it appears to be likely that there are also products of their reactions. Our further studies have revealed that Cys react with PLP *in vivo* forming Cys-PLP adduct which is presumably present in human plasma and remains to be novel metabolite[7]. These surprising results encourage further research into Cys-PLP, its presence in biological fluids and role as a potential marker of some cardiovascular diseases or reservoir of biologically active form of vitamin B6 in human body. These tasks remains to be the most challenging in near future.

Acknowledgement

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Quantitative determination of ergothioneine by HPLC/ICP-QQQ-MS

Nina Kroepfl[1], Talke A. Marschall[2], Kevin A. Francesconi[1], Tanja Schwerdtle[2] and Doris Kuehnelt[1]

[1] *Institute of Chemistry, NAWI Graz, University of Graz, Austria*
[2] *Institute of Nutritional Science, University of Potsdam, Germany*

Accurate analytical methods for the quantitative determination of ergothioneine are of interest due to the antioxidant activity and cytoprotective effects of this sulfur-containing species. A method using reversed-phase high performance liquid chromatography (RP-HPLC) coupled with elemental mass spectrometry detection was developed. To overcome the problems of interferences during the detection of sulfur, an inductively coupled plasma triple quadrupole mass spectrometer (ICP-QQQ-MS) was operated in mass shift mode using oxygen as a reaction gas, which enabled the determination of ergothioneine in complex biological matrices (human hepatocyte carcinoma cells (HepG2) and cell culture medium). Application of an instrumental setup using a 6-port-valve and the introduction of a methanol gradient allowed the time-efficient analysis of samples also containing strongly retained sulfur species without compromising the ICPMS detection.

In aqueous solutions, limits of detection and quantification (LOD and LOQ) for *m/z* 32 → 48 (SO^+) were 0.23 µg S L^{-1} and 0.80 µg S L^{-1}, respectively; measurements in the cell pellet matrix resulted in an LOD of 0.6 µg S L^{-1} and an LOQ of 2.3 µg S L^{-1}. Quantitative determination of ergothioneine was not impaired by sample preparation as shown by recoveries of ergothioneine from cell pellets spiked with the analyte before cell lysis (97 ± 3%) and cell culture medium spiked before syringe filtration (96 ± 9%). Low absorption of ergothioneine by the HepG2 cells was detected when cells were exposed to 1 mM ergothioneine present in the cell culture medium. Approximately 3% of the added ergothioneine was found in cell lysates, while most of it (≥ 85%) remained in the cell culture medium.

The method was successfully applied to the separation of ergothioneine from other biologically relevant sulfur-containing compounds, and is expected to be of broad future use. The possible simultaneous separation of several selenium-containing species will further extend its scope of applications.

Acknowledgement
We thank the Austrian Science Fund (FWF, project number I 2262-N28), the "Deutsche Forschungsgemeinschaft" (DFG, project grant number SCHW 903/9-1), the ''NutriAct – Competence Cluster Nutrition Research Berlin-Potsdam'' funded by the Federal Ministry of Education and Research (project number 01EA1408B), as well as the "Fonds der Chemischen Industrie" for financially supporting this work.

Dynamic of isomerization of Hop (*Humulus lupulus* L) alpha-acids in brewing process

Miha Ocvirk and Iztok Jože Košir

[1] *Slovenian Institute of Hop Research and Brewing,C. Žalskega tabora 2, SI-3310 Žalec, Slovenia*

Hop is considered, to be a key ingredient for beer flavour in brewing process. It contains bitter resins, named alpha-acids in lupulin glands, which are of crucial importance for beer bitterness. The most important chemical reaction in brewing process is a conversion of in water less soluble alpha-acids into soluble and bitter tasting iso-alpha-acids during wort boiling. The aim of this study was to determine the isomerization dynamic over the brewing process. Determination of alpha-acids and iso-alpha-acids was carried out according to Analytica EBC, method 9.47[1], using HPLC. The best isomerization yield (34.8 %) was achieved after 100 min of wort boiling, but the amount of iso-alpha-acids related to beer was even lower 27.9 %. Low isomerization percentage is a consequence of a low solubility of alpha-acids in water, and some other factors, such as adsorption on the trub, which are later removed in a clarification process[2].

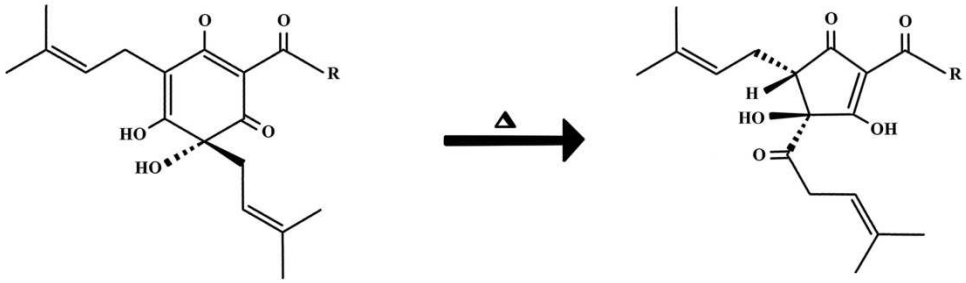

Fig. 1. Mechanism of alpha-acids isomerization into iso-alpha-acids

Acknowledgement
The authors would like to thank to the Slovenian Research Agency for the financial support of PhD student.

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A novel arsenolipid biosynthesised by Dunaliella tertiolecta under controlled culturing conditions

Ronald A. Glabonjat[1], Georg Raber[1], Kenneth B. Jensen[1], Klaus Zangger[1], Nikolaus Guttenberger[1], Josef Ehgartner[1], Elliott G. Duncan[2], Simon Foster[2], William A. Maher[2] and Kevin A. Francesconi[1]

[1] *Institute of Chemistry, University of Graz, Austria*
[2] *Institute for Applied Ecology, University of Canberra, Australia*

Lipid-soluble arsenicals, also called arsenolipids, have attracted significant interest in the last decade owing to their ubiquitous presence in many marine organisms and their currently unknown biosynthesis and possible biological role. We chose to investigate these processes in the arsenolipid-rich green alga, Dunaliella tertiolecta, and uncovered during our analyses an arsenolipid fundamentally different from all previously identified ones. This compound constituted ca 30-80 % of all arsenic lipids in D. tertiolecta grown under various laboratory culture conditions; the remaining lipid-arsenic mainly consisted of known arsenic-containing hydrocarbons and phospholipids. To elucidate the chemical structure of the new lipid, we isolated the compound and utilised a variety of analytical approaches including NMR spectroscopy and the coupling of HPLC to elemental and molecular mass spectrometry. We also performed a range of chemical derivatisations on the natural compound, and chemically synthesised several model compounds. Based on these experiments, we propose a structure for the new arsenolipid, and discuss its significance in biosynthesis and arsenic cycling.

Hyphenation of surfactant-free microemulsion electrokinetic chromatography (SF-MEEKC) with ESI-MS and UV detection for the determination of water- and fat-soluble neutral vitamins

Urška Mohorič[1], Mitja Kolar[1]and Frank-Michael Matysik[2]

[1] *Faculty of Chemistry and Chemical Technology, Večna pot 113, 1000 Ljubljana, Slovenia*
[2] *Institute of Analytical Chemistry, Chemo- and Biosensors, University of Regensburg, Universitätsstraße 31, 93053 Regensburg, Germany*

Microemulsion electrokinetic chromatography (MEEKC) is well-established analytical technique that enables separation of charged analytes based on their electrophoretic behavior and also neutral analytes based on their hydrophobic and hydrophilic properties. However, as a major drawback the conventionally used SDS based microemulsions are not compatible with electrospray ionization mass spectrometry (ESI-MS)[1]. In this work, a rather new generation of surfactant free microemulsions (SFME) consisting of water, ethanol and 1-octanol is used for surfactant-free microemulsion electrokinetic chromatography (SF-MEEKC). Electrophoretic separation was enabled with addition of ammonium acetate to the SFME. The stability of the ammonium acetate containing SFME was investigated using small-angle-X-ray scattering and dynamic light scattering[2,3]. A method separating a model system of hydrophobic and hydrophilic neutral vitamins was developed using UV/VIS detection and the ammonium acetate content was optimized. The method was characterized concerning reproducibility of migration times and peak areas and concerning the linearity of the calibration curve. Furthermore, SF-MEEKC was coupled to electrospray ionization mass spectrometry investigating compatibility between the new microemulsions and the ESI process. Finally, the vitamin D_3 content of a drug treating vitamin D_3 deficiency was determined with the ESI-MS detection, using 25-hydroxycholecalciferol as internal standard[4].

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Application of different extraction methods to characterize the Tonka bean extracts volatile profile

Silvie Surmová, Tomáš Bajer, Aleš Eisner and Karel Ventura

University of Pardubice, Department of Analytical Chemistry, Faculty of Chemical Technology, Studentská 95, Pardubice, CZ-53210 Czech Republic

Although tonka bean (*Dipteryx odorata* (Aubl.) Willd.) extracts are widely used, mainly in perfumery industry, research studies about volatile compounds of tonka beans are sporadic. This can be explained by the almost exclusive focus of researchers on the main compound coumarin, which is at the forefront of interest due to its toxicological properties. This study presents the results of the analysis of volatile compounds obtained from tonka beans using the various following extraction methods − headspace solid phase microextraction (HS-SPME), hydrodistillation (HD) and supercritical fluid extraction (SFE). Separation and identification of the compounds were carried out with a capillary gas chromatography setup connected to a mass spectrometer. A total of 191 compounds were identified and categorised into chemical groups. There were included 156 (HS-SPME), 77 (HD) and 36 (SFE) compounds (alcohols, carbonyl compounds, acids, esters, terpenes, terpenoids, lactones, aliphatic and aromatic hydrocarbons, and other non-categorised compounds). Coumarin was confirmed to be the main compound in Tonka bean, accounting for 51-85 % of the total content, depending on the extraction method. Extracts prepared by HS-SPME were richer in alcohols, carbonyls and acids content than extracts from other methods.

Natural antimicrobial substances and their use in the food industry

Simona Kučerová[1], Iveta Brožková[1] and Lenka Česlová[2]

[1] *Department of Biological and Biochemical Sciences, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic.*
[2] *Department of Analytical chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic*

Despite great advances in medicine and many scientific findings, foodborne infections and intoxications are still a major problem. These diseases are caused by the use of foods contaminated with bacteria or their toxins. In addition, the resistance of bacteria to a wide range of biocides used in food processing operations, has increased considerably in recent years. Finding new antimicrobials can help combat this problem.

It is well known that natural products are a source of the antimicrobial substances, and above all, go with today´s trend of using natural products. The aim of this study was to verify the survival of ten foodborne pathogens (*Listeria monocytogenes*, *Arcobacter butzleri*, *Campylobacter jejuni*, *Yersinia enterocolitica* etc.) in the presence of extracts from selected plants (cardamom, galangal, hop, licorice, sage, sea buckthorn and tarragon).

Plants (dried or fresh) were extracted in an ultrasonic bath into ethanol. Subsequently, suspensions were filtered and put into the thermostat. After complete evaporation, the dry extracts were dissolved in ethanol or distilled water. Sensitivity testing was performed by a disk diffusion method in three replicates.

All tested ethanolic extracts inhibited growth of some tested bacterial strains. The best inhibitory effects were measured for the ethanolic hop extract, which inhibited almost all the tested bacteria. On the contrary, the sage ethanolic extract inhibited growth only four bacterial strains. The inhibitory effect of aqueous extracts was lower, but some extracts suppressed the growth of bacterial strains, as well.

Now, HPLC analysis of the individual extracts is performed to determine the spectrum of substances contained in extracts. The next step will be to test the antimicrobial effect by a disk diffusion method of the individual compounds that occurred most frequently in the extracts, and then experiment on artificially contaminated real food.

Natural products are known to be a source of antimicrobial agents. If a further series of tests are carried out, the compounds contained in the plants have a great future as food additives with antimicrobial effects.

Acknowledgement
This study was supported by a grant project of the Faculty of Chemical Technology, University of Pardubice, Czech Republic (SGS 2017 004).

Voltammetric behaviour of mandelic acid – titanium(IV) – chlorate(V) system at the bismuth bulk electrode

Krystian Węgiel and Bogusław Baś

AGH University of Science and Technology, Faculty of Material Science and Ceramics, Department of Analytical Chemistry, Al. Mickiewicza 30, 30-059 Kraków, Poland

The aim of this work was to study the electrochemical properties of a catalytic adsorptive system of titanium(IV) – mandelic acid (MA) – chlorate(V) by means of differential pulse adsorptive stripping voltammetry (DP AdSV) using the bismuth bulk annular band electrode (BiABE)[1], activated *in situ* before each measurement. The method is based on the reduction of Ti(IV)-MA complex to Ti(III)-MA observed at the -0.85 V, followed by the reoxidation of Ti(III) to the Ti(IV) oxidation state in the presence of chlorate ions. Crucial point of the proposed procedure is simple and fast regeneration of the BiABE's surface in the presence of testing solution, by application of the activation potential (E_{act} = −1.7 V) and next short accumulation potential (E_{acc} = −0.5 V). Moreover, it was observed that the mandelic acid gives only one reduction signal at potential -0.62 V. The voltammetric behaviour of mandelic acid was investigated by cyclic voltammetry (CV). The experimental variables such as; potential and time of activation or accumulation, pH, concentration of the supporting electrolyte, DP mode parameters and influence of possible interferences on the Ti(IV) and mandelic acid signal response were tested.

Optimum conditions for DP AdSV determination of mandelic acid were achieved in 0.04 mol L^{-1} acetate buffer of pH 5.0 and for DP AdSV determination of Ti(IV) in 0.02 mol L^{-1} acetate buffer of pH 3.8. Finally, the proposed method was successfully applied for the determination of the Ti(IV) in the certified reference surface water and mandelic acid in almonds.

Acknowledgement
This work was supported by the Polish National Science Centre (Project No. 2015/19/B/ST5/01380).

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Application of Novel Tellurium Film Electrode for Copper(II) Determination by Means of Anodic Stripping Voltammetry

Julia Śliwa, Andrzej Bobrowski, Agnieszka Królicka and Jerzy Zarębski

AGH – University of Science and Technology, Department of Building Materials Technology, Faculty of Materials Science and Ceramics, Kraków, POLAND

Stripping voltammetry is one of the most sensitive analytical methods. The type of working electrode greatly affects the deposition of analytes and, consequently, the sensitivity of metal determination by means of anodic stripping voltammetry (ASV). The best analytical results have always been achieved using liquid mercury electrodes thanks to their excellent electrochemical performance; consequently, for many decades they were the type of electrodes applied most frequently in stripping voltammetry. However, restrictions connected with the toxicity of mercury have forced researchers to search for electrode materials that would replace mercury. The most popular bismuth and antimony metallic film electrodes developed in response to this challenge provide a wide range of useful potentials, mechanical stability, easily renewable surface and effective preconcentration in stripping procedures. However, the accessible potential windows of the majority of modern metal film electrodes are limited from the positive side due to the oxidation of the metal-forming film (e.g. Bi and Sb). To overcome this problem, a tellurium film electrode was applied to determine Cu in the present work. Therefore, the performance of a novel tellurium film electrode (TeF/GCE) deposited in situ on a glassy carbon (GC) support from an acidic solution is presented. A well-shaped and sensitive ASV response was achieved for copper. In the 0.1M HCl supporting electrolyte containing Te(IV), Cu(II) accumulated *in situ* with Te(IV) at the GC electrode provides an ASV peak at potential more positive than that obtained at a bare GC electrode by about 170 mV. Moreover, the SW-ASV peak of Cu obtained at the TeF/GCE is well-defined and ca. four times higher than the one recorded in the absence of Te(IV).

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The voltammetric determination of antioxidant – syringic acid

Justyna Robak, Barbara Burnat and Sławomira Skrzypek

University of Lodz, Faculty of Chemistry, Department of Inorganic and Analytical Chemistry, Tamka 12, 91-403 Lodz, Poland

Nowadays, the development of new electrode materials is a very important aspect in electrochemistry. For many years, the carbon based materials are very popular. One kind of the mentioned electrodes are carbon ceramic electrodes (CCEs). These materials are produced using sol-gel method in a very simple and fast way and can be easily modified in entire volume.

The CCEs can be used in voltammetric determination of antioxidants, for example syringic acid (SA). This compound can be found in several/different plants such as barley, maize, millet, oat, rice, rye, sorghum, and wheat. SA exhibits strong antioxidative and antiproliferative or anticancer activity. It plays an important role in maintaining human health, because it can neutralise free radicals and may prevent the cardiovascular disease.

In this study, the new voltammetric procedure for determination of syringic acid is presented. For that purpose the new type of carbon ceramic electrode modified in the entire volume with bismuth oxide nanoparticles was used. The voltammetric behaviour of syringic acid was investigated using square wave adsorptive stripping voltammetry (SW AdSV) Experimental conditions such as pH of supporting electrolyte, accumulation potential, accumulation time, and SW parameters were tested. Under the optimized conditions, the influence of syringic acid concentration on peak current value was estimated. The proposed electrode and developed SW AdSV procedure were successfully applied for determination of syringic acid in red wine and water samples.

Optimization of retinol extraction into the carbon paste electrode from milk samples

Simona Žabčíková, Milan Sýs and Libor Červenka

Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic

The aim of this study was optimization of extraction of retinol (vitamin A_1) into the carbon paste electrode (CPE)[1] from real milk samples. In our previous study[2], the extractive stripping voltammetry (ExSV) into glassy carbon paste electrode (GCPE) from 25% acetonitrile (ACN) was presented as suitable electroanalytical method for retinol determination. Nevertheless this contribution offers completely new approach (without ACN), where the extraction proceeds directly from milk sample followed by direct voltammetry in acetate buffer pH 4.5. Within optimization, different types of lipophilic binders such as paraffin oil, silicone oil, polypropylene, paraffin wax, and Vaseline were tested; moreover their content in CPE, and extraction time were investigated. Additionally, an adsorptive stripping voltammetry of other retinoids onto surface of solid glassy carbon electrode was preferred due to better shape of respective peaks which belong to irreversible process in selected acidic supporting electrolyte.

Acknowledgement
The support of the Faculty of Chemical Technology, University of Pardubice, (project No. SGFChT 2017/001) is gratefully acknowledged.

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Electrochemical study of the ionophoric antibiotic–monensin and its voltammetric determination in a forage for horses

Konrad Rudnicki, Monika Wrońska, Sławomir Domagała and Sławomira Skrzypek

Department of Inorganic and Analytical Chemistry, University of Lodz, Tamka 12, 91-403 Lodz, Poland

Monensin is a ionophoric antibiotic isolated in 1967 from *Streptomyces cinnamonensis.* It is widely used in ruminant animal feeds as a veterinary drug and growth promoter.

In presented work a rapid, sensitive, and new square-wave voltammetric (SWV) method using a renewable silver amalgam film electrode Hg(Ag)FE has been developed for the determination of monensin (*Mnz*, Fig.1). To select the optimum experimental conditions, the influences of the supporting electrolyte, pH, conditioning potential and time, frequency, amplitude, step potential, and equilibration time were investigated. The signal recorded at about -1.50 V (*vs*. Ag/AgCl/Cl^-) in Britton-Robinson buffer (pH 7.0) was used for analytical studies. At optimal conditions, the SWV response of Hg(Ag)FE for determining *Mnz* was linear over two concentration ranges of 7.5×10^{-8} to 5.0×10^{-7} mol L^{-1} and 5.0×10^{-7} to 1.0×10^{-5} mol L^{-1}. The limit of detection and quantification were 1.1×10^{-8} mol L^{-1} and 3.7×10^{-8} mol L^{-1}, respectively. The applicability of the developed method was tested by the determination of *Mnz* in the forage for horses samples by the standard addition method. In order to understand the *Mnz* electrode mechanism the cyclic voltammetry (CV) technique was applied.

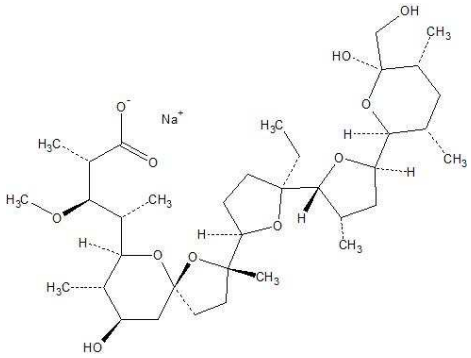

Fig. 1. The structure of *Mnz* monosodium salt.

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Electrochemical study of interactions between phytates and selected metal ions

E. Gričar, G. Marolt and M. Kolar

University of Ljubljana, Faculty of Chemistry and Chemical Technology, Večna pot 113, 1000 Ljubljana, Slovenia

Properties of phytic acid are known to be very complex due to high number of protons (12). However, the understanding of those properties is of high importance as phytic acid is one of the inositol phosphates and is as such often present in the cytosol and nucleus of eukaryotic cells.

In the presented research, the interactions between phytates and metal ions were studied using potentiometric titrations and cyclic voltammetry. When trying to determine the quantitative value of complex stability constants it is very important to know the exact concentration of phytic acid. In this work, a reliable alkalimetric determination of phytic acid is based on difference between certain equivalent points. Comparing their positions on the titration curve, one can also determine the initial protonation degree of phytate as well as type of contamination, if present.

The pH range, where different metal ions have a significant impact on acid–base properties of phytic acid, can also be determined from equivalent points' positions and shape of titration curve. These two parameters can also provide enough information for certain conclusions about phytate-metal complexes properties. Using different molar ratios of metal ions that are also present in the cytosol of eukaryotic cells one can observe the competition between different ions for binding sites on phytate. Cyclic voltammetry was carried out using molar ratio of phytate and iron(III) ions 1 : 20 at different pH values and different scan rates. Observing the position and height of peaks on voltammograms, one can determine complex stability and rate of formation.

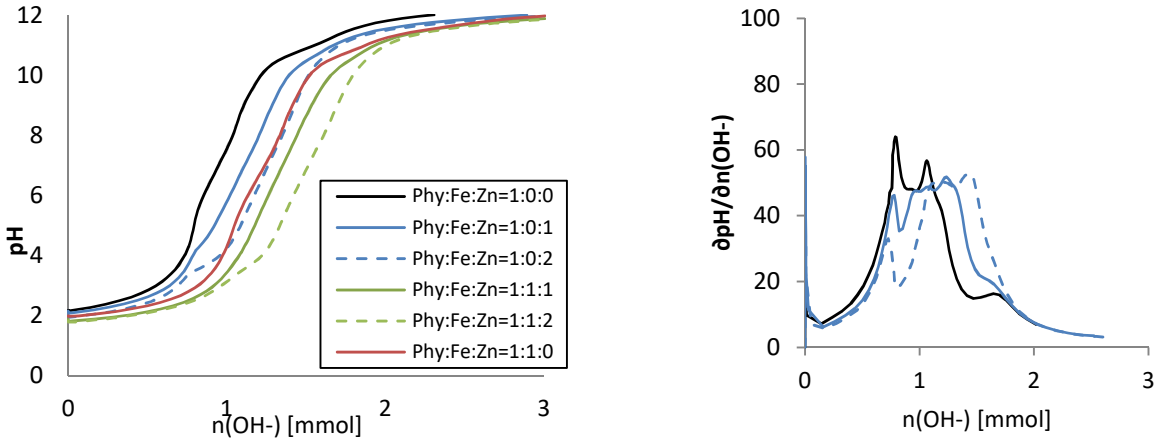

Fig. 1. *Left:* titration curves for various molar ratios Phy : Fe : Zn. *Right:* titration curve derivate versus quantity of NaOH consumed for titrations with zinc(II) ions

Deep Eutectic Solvents (DES): Green extraction of phenolic compounds from chokeberries (*Aronia melanocarpa*)

Milena Ivanović[1], Maša Islamčević Razboršek[1] and Mitja Kolar[2]

[1] *University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova ulica 17 SI-2000 Maribor, Slovenia*
[2] *University of Ljubljana, Faculty of Chemistry and Chemical Engineering, Večna pot 113 SI-1000 Ljubljana, Slovenia*

The new trends in the chemistry and the requirements for the environmental protection in the last few years lead to the increased interest for use of non-toxic, cheap and biodegradable solvents[1]. In this study, a novel analytical procedure based on deep eutectic solvents (DES) extraction and HPLC-UV analysis for the determination of selected phenolic compounds in the dried chokeberries (*Aronia melanocarpa*) was presented. In the first stage of the study, a simple HPLC-UV method for the simultaneous identification and quantitative determination of twenty one various phenolic compounds from different classes was developed and validated. Additionally, potential usefulness and effectiveness of DES as the „green“ alternative to the conventional organic solvents such as methanol, for the extraction of selected chokeberry phenols, were investigated. For that purpose five different DES based on choline chloride as the hydrogen bond aceptor in combination with different hydrogen bond donors (D-(-)-fructose, D-(+)-glucose, lactic acid and urea) were prepared. Recovery tests were performed on the *Aronia* samples spiked with target analytes. In the order to improve the extraction yield ultrasound assisted extraction (UAE) has been used. The results showed that the extraction recoveries of the compounds were highly dependent on the both, type of DES solvent as well as phenolic compound structures and ranged from 49.1% to 119%. Generally, fructose-based DES showed the highest capacity for extracting different phenolic classes from *Aronia melanocarpa* (even 33% higher than with 80% MeOH under the same extraction conditions). These results are certainly promising and they suggest future use of environmentally friendly and efficient DES solvents for the extraction of bioactive compounds from different plant materials.

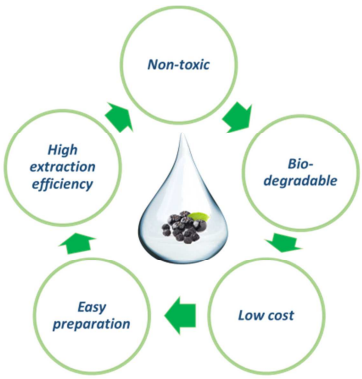

Fig. 1. The main properties of the novel Deep Eutectic Solvents (DES).

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The comparison of anthocyanin and pyranoanthocyanin extraction efficiency in Pinot Noir wine using SPE

Jelena Topic[1], Dorota Korte[1]and Branka Mozetic Vodopivec[2]

[1] *University of Nova Gorica, Laboratory for Environmental and Life Sciences, Nova Gorica, Slovenia*
[2] *University of Nova Gorica, Wine Research Centre, Vipava, Slovenia*

The colour in wine is associated with the presence of phenolic pigments named anthocyanins. Malvidin-3-glucoside and its derivatives are the most representative anthocyanins in grapes and wine and are most abundant in free form in young red wines. During the wine storage and ageing these pigments are replaced by other anthocyanin-derived pigments. Pyranoanthocyanins are currently acknowledged as one of the most important derivatives crucial for the stability of colour, especially in the wines that are known to be less rich in anthocyanin pigments like Pinot Noir[1]. HPLC/UHPLC techniques are widely used for separation and quantification of anthocyanins and its derived pigments. In case of wines, because of the complexity of chromatograms, it is sometimes necessary to perform prior step of sample preparation for cleaning and pre-concentration reasons, especially in the case of low concentrations of these compounds in real samples that can be masked by sample matrix, which is a huge problem in food/wine samples. The most widely used sample preparation steps are liquid-liquid extraction (LLE) and solid-phase extraction (SPE)[2-4].

The aim of our research was analysis and comparison of anthocyanin and pyranoanthocyanin profiles in wine Vitis vinifera Pinot Noir (vintage 2013 and 2015). For the purpose of this study, different conventional SPE cartridges were assessed (Oasis HLB, Phenomenex Strata-X, Phenomenex Strata C18, Isolute Env+, Phenomenex SDB-L, Oasis MCX). The cartridges were evaluated for efficiency of anthocyanin and pyranoanthocyanin extraction. The recovery of standard malvidin-3-glucoside was also assessed. The samples were analysed with RP-HPLC-DAD method. For identification and quantification external standard malvidin-3-glucoside was used. As commercial standards for most of the pyranoanthocyanins do not exist, UV-Vis spectra and retention times from Wine Research Centre's database were used for their identification.

The results showed that extraction efficiency differs depending on the cartridge used and elution solvent used. Results also showed that anthocyanin and pyranoanthocyanin profile and concentration differs with wine age. In order to obtain better recoveries, further elution solvent optimisation is needed.

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Determination of bitter acids in various hop species and evaluation of their contents in beer prepared by so-called dry hoping

Karolína Adámková[1], Martin Adam[1], Aleksander Poreda[2], Jonas Trummer[2] and Monika Cioch[2]

[1] *Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice*
[2] *Department of Fermentation Technology and Technical Microbiology, Faculty of Food Technology, University of Agriculture in Krakow, Balická 122, 30-149 Kraków*

The aim of this work was to determine the content of α- and β-bitter acids commonly found in hops. A total of 7 different hop varieties were analysed. The results were compared with the data provided by the distributor. Determination of bitter acids was performed by HPLC method with UV-VIS detection at 314 nm after extraction of hop pellets according to the standardized EBC method (7.7), which used ICE-3 (International Calibration Extract 3) as a hop extract containing a specified concentration of α- and β-acids[1]. The pattern of the ICE-3 chromatogram is shown in the Figure 1. Finally, there were analysed some real samples of beers brewed using so-called dry hoping process. Extracts from beers were prepared by the same way as extracts from hop pellets. Obtained results were evaluated and there were investigated if it is possible to determine the content of bitter acids (assumed before isomerisation) after dry hoping. Beer samples were also brewed by our own technology at the university brewery where the Perle hop was used for dry hoping.

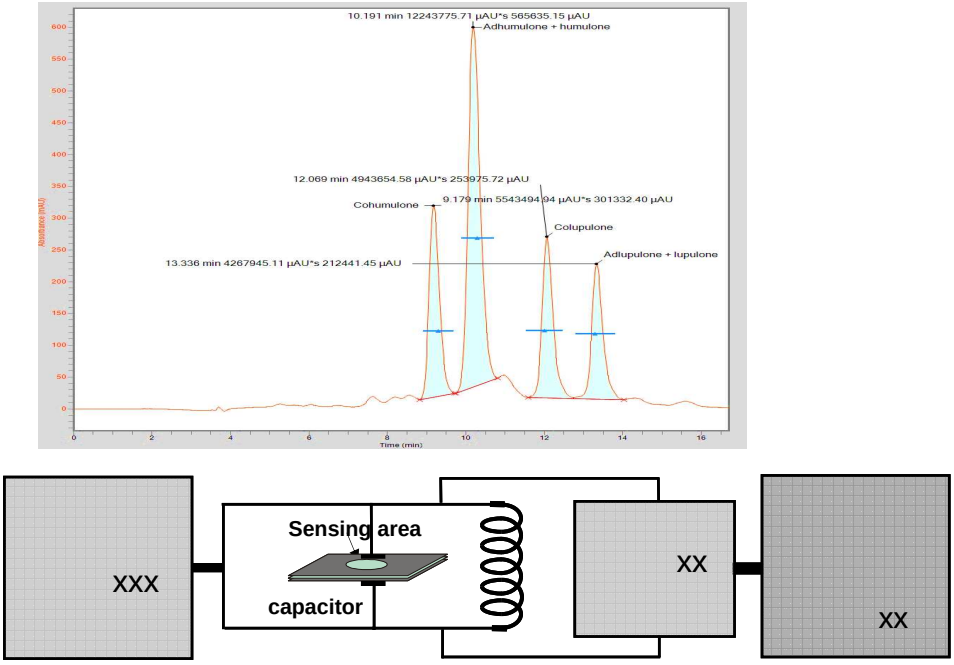

Fig. 1. Chromatogram of ICE-3 hop extract containing standard substances (peak 1: Cohumulone, peak 2: Adhumulone + Humulone, peak 3: Colupulone and peak 4: Adlupulone + Lupulone).

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Support is acknowledged for Erasmus+ programme (higher education traineeship), which allowed me to internship in Kraków, Poland (1.3. – 1.6. 2017).

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Analysis of Neonicotinoid Pesticides in Honey

Miha Mrzlikar[1], David Heath[2], Ester Heath[2,3], Jernej Markelj[1] and Helena Prosen[1]

[1] *Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, 1000 Ljubljana, Slovenia*
[2] *Department of Environmental Sciences, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia*
[3] *Jožef Stefan International Postgraduate School, Jamova cesta 39, 1000 Ljubljana, Slovenia*

Neonicotinoid pesticides are used to provide in-plant protection from insects for a period during plant establishment. Although originally considered safe in the environment, their use has been linked to honey-bee colony collapses. In 2013, the European Commission imposed a temporary ban on the use of the three key neonicotinoids (clothianidin, imidacloprid, thiamethoxam) on crops attractive to bees. Additionally, in March 2017 the EU proposed a complete ban of the three neonicotinoids from all fields, except for use in permanent greenhouses. There has been an increased interest in determining neonicotinoid residues in honeybee products and bees, but according to our data very little has been done on neonicotinoids concentration in Slovenian honey.

The aim of this study was to develop a reliable analytical method in order to monitor the presence of five neonicotinoid pesticides (acetamiprid, clothianidin, imidacloprid, thiacloprid, thiamethoxam) in Slovenian honey. In order to do that, we compared two different extraction techniques (Solid Phase Extraction and QuEChERS) in terms of extraction efficiency, matrix removal, repeatability, limit of detection (LOD), and limit of quantification (LOQ). We used matrix-matched calibration to compensate for the matrix effects. The analyses were carried out using LC-MS/MS in selected reaction monitoring (SRM) mode. Validation was performed at two spiking levels (10 µg/kg and 50 µg/kg) with three replicates at each level. Both sample pretreatment procedures showed satisfactory recoveries (68.2–113.6 %) and precision (RSDs between 0.9–8.0 %), low limits of detection (0.05 to 0.97 µg/kg) and quantification (0.19 to 3.25 µg/kg) for all analytes. QuEChERS extraction was more efficient in matrix removal than SPE, which was expressed as the slope ratio between matrix-matched calibration and solvent calibration. Both methods are similar in time-consumption (approximately 40 min/sample), but the QuEChERS method is slightly cheaper than SPE. The validated QuEChERS method using LC-MS/MS was applied for the analysis of 50 honey samples (28 floral, 15 forest, 5 acacia, 2 linden), which were systematically collected from different regions of Slovenia. The research revealed the presence of acetamiprid and thiacloprid in some samples in low amounts. No analyte exceeded the maximum residue levels (MRLs), which showed that the contamination of Slovenian honey with neonicotinoid pesticides is negligible.

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Distribution of arsenic and its species in human milk

Michael Stiboller[1], Georg Raber[1], Virissa Lenters[2], Elin Lovise Folven Gjengedal[3], Merete Eggesbø[2] and Kevin A. Francesconi[1]

[1] *Institute of Chemistry, NAWI Graz, University of Graz, Austria*
[2] *Norwegian Institute of Public Health, Oslo, Norway*
[3] *Norwegian University of Life Sciences, Faculty of Environmental Sciences and Natural Resource Management, Ås, Norway*

The toxicity of arsenic depends on its chemical form, with inorganic arsenic being highly toxic to humans whereas organic arsenic compounds are generally considered much less so, and thus risk assessment of arsenic exposure must consider the type of arsenic compound. Furthermore, because risk assessments need to include the most vulnerable persons within a population, such as newborns and infants, estimation of the arsenic species in human milk is needed. As part of the Norwegian HUMIS-NoMIC birth-cohort study on the effects of environmental toxicants on the neuropsychological development in children, we aimed to determine trace levels of arsenic and arsenic species in human milk samples by using ICPMS and HPLC/mass spectrometry. Herein, we describe a novel sample preparation procedure developed to measure the distribution of arsenic in both the aqueous and lipid phases of human milk, and report preliminary data on the types of arsenic species present in 297 milk samples from the HUMIS-NoMIC study.

Metabolomics for characterizations of officinal herbs: the case of *Helichrysum* species

Giovanni Rizzato, Marta Radaelli, Elisa Scalabrin, Giuseppa Toscano and Gabriele Capodaglio

Department of Environmental Sciences, Informatics and Statistics, University of Venice, Ca' Foscari, Via Torino 155, 30170, Mestre, VE, Italy.

Helichrysum is a widespread and heterogeneous genus (about 600 species) of the Asteraceae family, well known in various part of the world for their biological properties, like antioxidant, antimicrobial and anti-inflammatory, and have been used in traditional medicine for at least 2000 years. These properties are due to the accumulation of phenolics (flavonoids and non-flavonoid) compounds in many parts of the plant. One of the most studied species in the Mediterranean area is *H. italicum*, but many others are used and not so well studied. The metabolic characterization is fundamental for quality control in food, supplements and drugs production and to try to correlate the officinal properties of a plant with a compound or a specific class of substances.

In this work, three different samples of different parts (flowers and stems) of *Helichrysum* species (*H. italicum*, *H. stoechas*, *H. hyblaeum*) from Sicily, were analysed using a metabolomic approach. *H. hyblaeum* is endemic of Sicily and very few data are available in the literature, especially regarding its metabolic composition. The aim of this work is to characterize and elucidate the metabolic differences among three species of the same area, proposing new biomarkers especially for the unstudied species *H. Hyblaeum*.

The analyses were performed using HPLC (High Performance Liquid Chromatography) coupled with HRMS (High Resolution Mass Spectrometry). The LTQ Orbitrap XL system assures great mass accuracy and high resolution allowing to acquire a comprehensive metabolic profile of the samples. The analyses were conducted in full scan mode, at a resolving power of 60000, with a mass range between 90 and 1500 m/z.

Using statistical and chemometric methods (Analysis of Variance, Cluster analysis and Principal Component Analysis), the main differences among species were highlighted.

Investigation of thiacloprid removal from water media by magnetite modified multiwalled carbon nanotubes

Ana Tasić[1], Maja Polić[1], Mónika Kalmár[1], Miroslava Jovanović[1], Valéria Guzsvány[1], Olga Vajdle[1], Laszló Nagy[2], Ákos Kukovecz[2] and Zoltán Kónya[2]

[1] *University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovića 3, 21 000 Novi Sad, Serbia*
[2] *University of Szeged, Department of Applied and Enviromental Chemistry, Rerrich Béla tér 1, 6720 Szeged, Hungary*

Neonicotinoids are worldwide applied representatives of the relative new generation of insecticides which act on the level of the nicotinic-acetylholine receptors of the target insects[1,2]. Due to the increase of their presence in the environment, they become a potential risk. One of the most stable of them in aqueous media is thiacloprid (TIA)[3] from the first generation of neonicotinoids. The aim of this work is to investigate the possibility of removal of TIA from the aqueous media by suspended particles of multiwalled carbon nanotubes (MWCNT) modified with 2.5% and 10% magnetite (2.5%Fe_2O_3-MWCNT and 10%Fe_2O_3-MWCNT). The investigations were performed by different weight of both nanomaterials as 5, 10, 15 and 20 mg which were suspended in 20.0 mL of bidistilled water. Additionnaly, in the case of the 10%Fe_2O_3-MWCNT composite and the basic MWCNT materials (5 mg in all cases) H_2O_2 was added into the system at two concentration levels as 59 µg/mL and 106 µg/mL for the investigation of the behavior of the Fenton like systems. In all investigated cases the initial concentration of TIA was 2.4 µg/mL. The TIA removal was monitored by a simply HPLC-DAD method from the water phase of the samples which were taken at following time intervals: 0.0; 1.0; 2.5; 5.0; 7.5; 10.0; 15.0; 20.0; 30.0 and 40.0 min from the bulk of the magnetic stirrer mixed sample by syring injection. Such samples were immediately filtered via hydrophylic syring filters 0.22 µm and deeply frosen. They tempered to the room termerature only before the HPLC measurements. It was found that the amount of the used nanomaterials influences significantly the TIA removal and the magnetic behavior of the composite material helped for the removal of adsorbents. The most intensive changes in the TIA concentration were observed in the first 5 min of the contact time. The both magnetite modified nanocomposites can serve as effective adsorbens which allowing almost total removal under optimzied experimental conditions. In the case of the systems with H_2O_2 the 5 mg of the 10%Fe_2O_3-MWCNT is appropriate for fast removal of TIA, but a degradation intermediate was observed in the water phase of the system.

Acknowledgement
Financial support of the projects of Minstry of Education, Science and Technological Development of R. Serbia ON172059, ON172012 and CEEPUS CIII-CZ-0212-09-1516 is greatfully acknowledged.

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Multi-biomarker analysis of sediments for paleoclimate research

Alice Callegaro[1], Torben Kirchgeorg[1], Elena Argiriadis[1], Dario Battistel[1], Natalie M. Kehrwald[2], Broxton W. Bird[3] and Carlo Barbante[1,4]

[1] *Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, 30172 Venezia, Italy*
[2] *U.S. Geological Survey, Geosciences and Environmental Change Science Center, Denver, CO 80225, USA*
[3] *Department of Earth Sciences, Indiana University-Purdue University, Indianapolis, IN 46208, USA*
[4] *Institute for the Dynamics of Environmental Processes (IDPA-CNR), 30172 Venezia, Italy*

Lacustrine sedimentary cores provide continuous records of large-scale and local environmental modifications, intelligible thanks to specific organic markers that accumulated in these archives during past millennia. In order to improve our knowledge on ecosystem changes due to biomass burning events and human presence during the Holocene, an effective analytical method to detect organic compounds contained in sediment samples is needed.

We used Accelerated Solvent Extraction (ASE) technique followed by analysis with gas and liquid chromatographers coupled with mass spectrometers (GC-MS, IC-MS). The extraction of the molecules of interest from the sediments is made with a mixture of DCM:MeOH 9:1 v/v and it is followed by a 3 steps purification with silica gel columns. The first fraction is eluted with HEX:DCM 9:1 v/v and contains n-alkanes, indicators of vegetation, and polycyclic aromatic hydrocarbons (PAHs) as combustion proxies. Then, a second fraction is eluted with DCM and derivatized with the silylation process, in order to get the faecal sterols and stanols (FeSts), indicators of past human and grazing animals presence. These two fractions are analysed with the GC-MS technique. The third and last fraction is eluted with MeOH and contains the monosaccharide anhydrides (MAs), specific indicators of vegetation burning processes, which are analysed with IC-MS. Internal standards labelled C13 are used for the quantification and procedural blanks are extracted every batch of 12 samples.

The method may undergo variations, on the basis of the complex sediment matrices which not always lend itself to the same kind of treatment. However, the technique was applied in different lakes from different continents and the obtained results, compared with historical and climate literature data, seem to demonstrate the potentiality of the method as a resourceful instrument to reconstruct past burning events and human-ecosystem interactions.

Development of a hollow fibre microextraction method for determination of benzotriazoles

Ida Kraševec and Helena Prosen

University of Ljubljana, Faculty of Chemistry and Chemical Technology, Večna pot 113, Slovenia

Benzotriazoles are heterocyclic compounds, used as corrosion inhibitors in different industrial processes and as UV stabilizers in plastics. They are classified as emerging pollutants due to their harmful effects on plants and toxicity to some aquatic organisms, can be only partially removed from water in wastewater treatment plants and are therefore found in various environmental samples in concentrations ranges of µg/L. Their determination demands the use of preconcentration techniques, most commonly solid-phase extraction (SPE) with different types of sorbents, combined with sensitive analytical techniques, such as LC-MS/MS[1].

Hollow fibre microextraction (HFME) is an alternative type of liquid-liquid extraction, where only small amounts of organic solvents are used in combination with porous polypropylene fibres. The analytes from donor phase or sample are extracted into the organic solvent immobilized in the pores of the membrane, and further concentrated in the acceptor phase inside the lumen of the fibre, which can be either an organic solvent or an aquatic solution. The main advantages of this technique in comparison to other microextraction techniques are its high selectivity and good enrichment factors[2].

In this work, a HFME method was developed for the extraction of benzotriazoles from water samples, which included the optimization of the following parameters for the 3-phase type of extraction: selection of solvent, pH of donor and acceptor solutions, ionic strength of donor phase, fibre length, time of extraction and stirring speed. The optimal conditions included the use of 1-octanol as solvent, acidic donor and basic acceptor solution, presence of NaCl in 10 ml of sample and the extraction time of 50 min at stirring speed of 1000 rpm with fibre length of 10 cm. At these conditions, the enrichment factors for six analysed polar benzotriazoles ranged from 42 to 152, with correlation to their polarity.

All extracts were analysed with a previously developed HPLC-UV method.

Acknowledgement

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Determination of ionic compounds in Antarctic samples using ion-chromatography coupled to mass spectrometry

Sara Padoan[1], Elena Barbaro[1], Roberta Zangrando[2], Gabriele Capodaglio[1], Carlo Barbante[1,2] and Andrea Gambaro[1,2]

[1] *Department of Environmental Sciences, Informatics and Statistics, University of Venice, Ca' Foscari, Via Torino 155, 30170, Mestre, VE, Italy.*
[2] *Institute for the Dynamics of Environmental Processes CNR, Via Torino 155, 30170 Mestre,VE, Italy.*

The aim of the present work was to develop an analytical method for the quantification of anionic and cationic compounds (Cl^-, Br^-, I^-, NO_3^-, MSA, SO_4^{2-}, PO_4^{3-}, C_2-oxalic acid, C_2-glycolic acid, C_2-acetic acid, C_3-malonic acid, cis-usC_4-maleic, trans-usC_4-fumaric, C_4-succinic acid, αC_7-benzoic acid, C_5-glutaric acid, hC_4-malic acid, C_6-adipic acid, C_7-pimelic acid, Na^+, NH_4^+, K^+ and Mg^+) to determine their potential sources of input, chemical evolution and transport in aerosol Antarctic samples[1].

We analysed anionic species using ion-chromatography coupled to mass spectrometry and cationic species by capillary ion-chromatography with conductivity detection. The methods were validated through the evaluation of the instrumental linearity, detection limits and instrumental precision; and recovery, accuracy and repeatability of the analytical sample preparation procedure.

We determined concentration and particle-size distribution of ionic species from two different Antarctic site: a coastal site near to the Italian Research Station “Mario Zucchelli” and a site located on the Antarctic plateau, close to the Italian-French Research Station “Concordia”.

We evaluated possible sources of marine aerosol and behaviour during long distance transport. Aerosol, from the coastal site, was mainly characterized by sea salt species such as Na+, Mg^{2+}, SO_4^{2-}. These species were mainly distributed in the coarse fraction, confirming the presence of primary aerosol near the ocean source.

Aerosol collected over the Antarctic plateau was characterized by species as nss-SO_4^{2-}, NO_3^- and methanesulfonic acid. These species were mainly distributed in the fine fraction, highlighting a behaviour of a typical secondary aerosol, where several chemical and physical processes occurred.

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Production and characterization of whey peptides bioactive in a packed bed reactor (PBR)

Clariana Zanutto Paulino da Cruz[1], Ariela Veloso de Paula[2], Rubens Monti[2] and Gabriella Massolini[3]

[1] *São Paulo State University (UNESP), Chemistry Institute - 14800-060, Araraquara, SP, Brazil.*
[2] *São Paulo State University (UNESP), Faculty of Pharmaceutical Sciences - 14800-903, Araraquara, SP, Brazil*
[3] *Università degli studi di Pavia. Dipartimento di Scienze del Farmaco - 27100, Pavia, PV, Italy.*

The production of bioactive peptides by enzymatic hydrolysis can be staggered at industrial levels using enzyme-based bioreactors. A packed bed reactor (PBR) based on alcalase glyoxyl corn cob powder (AGCCP) was successfully developed for the enzymatic hydrolysis of bovine cheese whey for the production of bioactive peptides. PBR, containing 25 g of AGCCP was run at a flow rate of (6 $mL.h^{-1}$) and presented spatial time (12.9 h) approximately 19% higher than the calculated value (10.8 h). No preferential path formation across the bed was observed. Continuous hydrolysis of the whey proteins using AGCCP (8.66 U/g) occurred during 180 hours of reaction carried out at 50°C and pH 9.0. The system presented a high degree of hydrolysis (58.98-70.70%). The hydrolysis products were analyzed by RP-HPLC and MALDI-TOF analysis. The obtained bioactive peptides presented low molecular weight (<2600 m/ z) and high antioxidant capacity (65.27% ABTS reduction). The new developed process may be a viable strategy for food and pharmaceutical industry, as it allows the treatment and reuse of the whey for the production of antioxidant peptides.

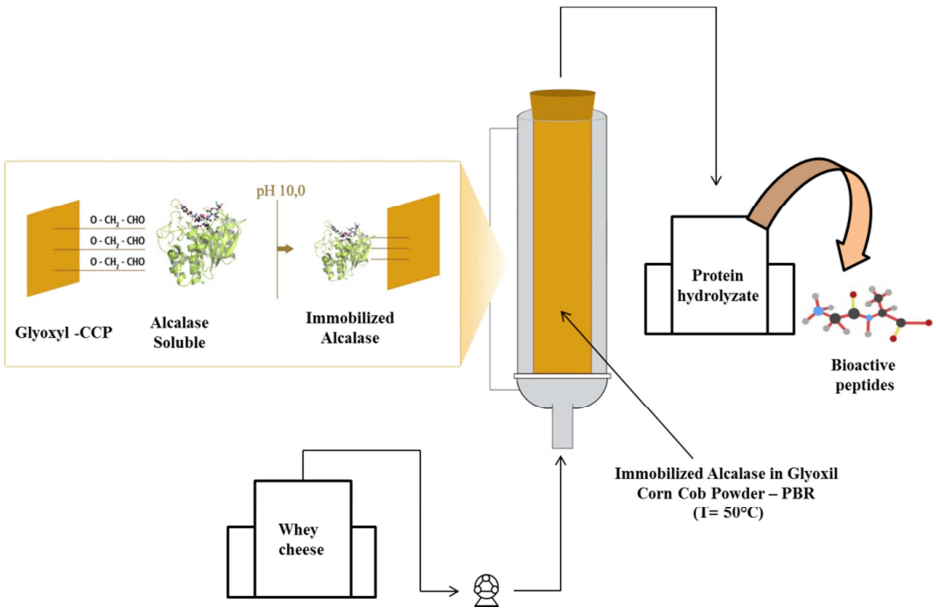

Fig. 1 PBR for enzymatic hydrolysis of whey proteins and the production of bioactive peptides.

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The influence of selected oxide pigments on drying of linseed oil

Urška Zupančič and Irena Kralj Cigić

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, SI-1000 Ljubljana, Slovenia

Linseed oil is one of the most broadly used drying oils in paints due to its fast drying[1]. However, drying of linseed oil is a complex process, which includes autoxidation of oil followed by polymerization. It is influenced by different parameters that are difficult to control: light, moisture, heat, atmospheric pollutants. Pigments in oil paints can also affect the drying process of oil by catalysis of chemical reactions in the autoxidative process[2-4].

The effect of four oxide pigments (Fe_2O_3, Cr_2O_3, TiO_2 and ZnO) on drying of linseed oil films was studied. Mixtures of pigment with linseed oil were applied on canvas and exposed to different conditions: to constant temperature of 60°C in the dark, to room temperature in the dark, to indoor laboratory conditions or to irradiation with xenon lamp. The degree of oil oxidation was monitored by fatty acids composition in the mixture by GC-MS, which is a reliable and highly sensitive method. The effect of Fe_2O_3 and Cr_2O_3 amount in the linseed oil on drying at a constant temperature of 60°C was also examined.

Results show that the amount of unsaturated fatty acids (linoleic and linolenic) in all paint films decreases with time due to oxidation of linseed oil. Rate of drying of oil paint is affected by the chemical structure and amount of pigment in paint and by the conditions of drying. It was confirmed that light and higher temperature accelerate autoxidation of linseed oil and consequently, increase drying rate of oil paint.

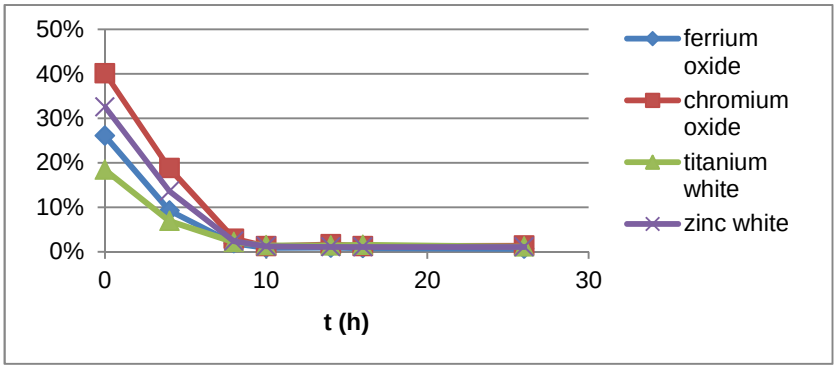

Fig. 1 Changing of relative percent of chromatographic peak area for methyl ester of linolenic acid in paint films treated at a constant temperature of 60 °C in the dark (10 % of pigment).

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Voltammetric determination of macrolide antibiotic azithromycin in the pharmaceutical preparation by carbon paste electrode surface modified with gold nanoparticles

Olga Vajdle[1], Nataša Bosnić[1], Valéria Guzsvány*[1], Milka Avramov-Ivić[2], Slobodan Petrović[3], László Nagy[4] and Zoltán Kónya[4]

[1] *Department of Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad, Trg D. Obradovića 3, 21000 Novi Sad, Serbia*
[2] *ICTM, Institute of Electrochemistry, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia*
[3] *Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia*
[4] *Department of Applied and Environmental Chemistry, University of Szeged, Rerrich Béla tér 1, 6720 Szeged, Hungary*

Azithromycin (AZI) is semi-synthetic macrolide antibiotic derived from erythromycin and in its structure contain 15-membered lactone ring[1]. AZI was determined by environmental friendly and low cost carbon paste electrode (CPE)[2], constituted only from graphite powder and paraffin oil, which is surface modified by drop coating method with gold nanoparticles with diameter of 10 nm (Au-CPE).

Voltammetric characterization of AZI was performed in aqueous solution of Britton-Robinson buffer, as supporting electrolyte, from pH 2.0 to pH 12, by Au-CPE and differential pulse voltammetry (DPV) in the potential range from 0.20 V to 1.10 V vs. saturated calomel electrode (SCE). At pH higher than 5.0 one oxidation peak was obtained with peak maxima in the potential range from 0.62 V to 0.85 V, depending on the pH value. Based on the peak shape and intensity, pH 12 with E_p 0.62 V vs. SCE was chosen as optimal pH value for analytical purposes. Investigation of the applicability of the square wave voltammetry (SWV) for determination of AZI by Au-CPE at pH 12 showed that by applying of SWV method the peak intensity of AZI is higher than in the case of DPV method and because of that in further determination of AZI the SWV method was used. The linearity of the calibration curve obtained by SWV method and Au-CPE was in the concentration range 0.15-3.84 μg mL^{-1} and the reproducibility of the analytical signal was characterized by the relative standard deviation (RSD) which is 3.4%. Applying SWV method and unmodified CPE lower limit of detection was observed, but using Au-CPE the linearity of analytical method is twice wider in comparison with CPE based method and the RSD is lower in the case of Au-CPE based method.

Developed SWV method using Au-CPE was successfully applied for determination of AZI in pharmaceutical preparation Hemomycin® by standard addition method. The average value for three determinations defined the AZI content as 249.5 mg/tablet with RSD of 0.8% which is very close to the content declared by the manufacturer as 250 mg/tablet.

Acknowledgement
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Comparison Study of Voltammetric Determination of Mesalazine Using Boron-doped Diamond Electrodes with Different Content of Boron

Michaela Štěpánková[1], Renáta Šelešovská[1], Lenka Janíková[1], Marián Marton[2] and Pavol Michniak[2]

[1] *University of Pardubice, Faculty of Chemical Technology, Institute of Environmental and Chemical Engineering, Studentská 573, 532 10 Pardubice, Czech Republic,*
[2] *Slovak University of Technology in Bratislava, Faculty of Electrical Engineering and Information Technology, Institute of Electronics and Photonics, Ilkovičova 3, 812 19 Bratislava, Slovak Republic.*

Mesalazine (5-amino-2-hydroxybenzoic acid, Fig. 1) is well-established compound used in the management of inflammatory bowel disease (IBD). Mesalazine is an active moiety of sulfasalazine drug, which is metabolized to sulfapyridine and mesalazine. Mesalazine, as an antioxidant, traps free radicals, which are potentially damaging by products of metabolism[1,2].

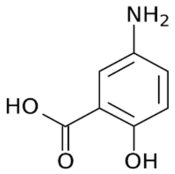

Fig. 1 The structure of mesalazine

The pure diamond is distinguished by outstanding mechanical and chemical stability and it is one of the best natural insulators. For its electrochemical utilization, it needs to be doped with atoms of other elements, most often with boron. Boron-doped diamond electrode (BDDE) has been firstly described in the eighties of previous century[3]. It is substantiated by its superior physical, mechanical, and electrochemical properties, such as wide potential window, thermal conductivity, chemical stability, and stable and low background current. The boron content in BDD is one of the factors influencing substantially the film conductivity and morphology. The concentration of boron also significantly influences the electrochemical properties of the BDD films. Obviously, increased boron content leads to higher capacitance, slightly narrower solvent windows, and can increase the likelihood of undesirable incorporation of sp^2 impurities[4]. In this study, mesalazine drug was used for investigation and comparison of application possibilities of BDDE with different content of boron.

Acknowledgement
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Preparation, characterization, and electrochemical application of ultra-trace graphite electrode modified with nanomaterials

Karolina Sipa, Mariola Brycht, Andrzej Leniart, Kinga Kaczmarska and Sławomira Skrzypek

University of Lodz, Faculty of Chemistry, Department of Inorganic and Analytical Chemistry, Tamka Str. 12, 91-403 Lodz, Poland

One of the most popular and most frequently used allotropic form of carbon is graphite. Thanks to its properties, it has found a wide range of applications in daily life as well as in electrochemistry. Graphite-based working electrodes, such as: graphite paste electrodes, pencil graphite electrodes, pyrolytic graphite electrodes, are commonly used in electroanalysis of many organic compounds. A relatively new type of graphite-based electrode is a ultra-trace graphite electrode (UTGE), which has been used so far for the voltammetric determinations of just a few analytes.

Nanomaterials, such as graphene nanoplatelets (GNP) and multi-walled carbon nanotubes (MWCNT) possess many advantages, like excellent conductivity, large surface area and electrocatalytic activity. Due to these properties they have been successfully incorporated into electrochemical sensors.

Metobromuron (*Mbn*) is a selective, systemic, pre-emergence herbicide currently approved for use in the EU. *Mbn* is adsorbed by the roots and leaves of annual broadleaved weeds and grasses. It has a low mammalian toxicity but has a high potential to bioaccumulate. *Mbn* is applied in fields of common beans, potatoes, tomatoes, tobacco, maize and sugar beet.

In the present work, bare UTGE, MWCNT-UTGE and GNP-UTGE were considered as working electrodes. The comprehensive microscopic and electrochemical characterization of proposed unmodified UTGE and modified electrodes was performed by atomic force microscopy (AFM) and cyclic voltammetry (CV), respectively.

The prepared electrodes were further applied for the analytical purposes. The procedure for the determination of pesticide *Mbn* using bare UTGE, MWCNT-UTGE and GNP-UTGE as a working electrodes was developed in square–wave voltammetric (SWV) measurement mode. Analytical signal was obtained at potential about +1.2 V on each electrode. The measurements were performed in Britton-Robinson buffer at pH 2.0 as a supporting electrolyte. SWV parameters, i.e. amplitude, frequency, and step potential, were optimized. The linear relationships between peak current vs. increasing concentrations of *Mbn* were defined using bare UTGE, MWCNT-UTGE and GNP-UTGE, and the limits of quantification and detection were calculated. The obtained results showed that GNP-UTGE possess advantages in terms of linearity, sensitivity and detectability when compared to bare UTGE, MWCNT-UTGE.

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Surface and electrochemical characterization of boron-doped diamond electrodes with different content of boron

Pavlína Martinková[1], Renáta Šelešovská[1], Jaromíra Chýlková[1], Marian Vojs[2] and Miroslav Behúl[2]

[1] *Institute of Environmental and Chemical Engineering, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic*
[2] *Institute of Electronics and Photonics, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology, Ilkovičova 3, 812 19 Bratislava, Slovak*

This study is focused on comparison of lab-made boron doped diamond electrodes (BDDE) with different content of boron prepared by hot filaments chemical vapor deposition. These electrodes have been characterized to their surface and electrochemical properties. Surface characterizations were provided by Raman spectroscopy and scanning electron microscopy. Their physical, chemical and electrochemical properties were investigated by using electrochemical impedance spectroscopy and cyclic voltammetry with the reversible redox markers $[Fe(CN)_6]^{3-/4-}$ (Fig. 1) and $[Ru(NH_3)_6]^{3+/2+}$. From these characterizations, the important characteristics of the recorded curves as differences between anodic and cathodic peak potentials (ΔE_p), anodic and cathodic peak heights (I_a, I_c), the ratios of I_a/I_c, etc., were found. At the end, all BDDEs were applied for determination of drug dantrolene, to compare obtained statistical parameters and to find out as behavior of these electrodes exhibits some trends in relation to the boron content. Results showed that with changing concentration of boron the electrochemical properties have been changing and proved that the content of boron in the diamond film significantly influences the electrochemical properties of the prepared electrode material.

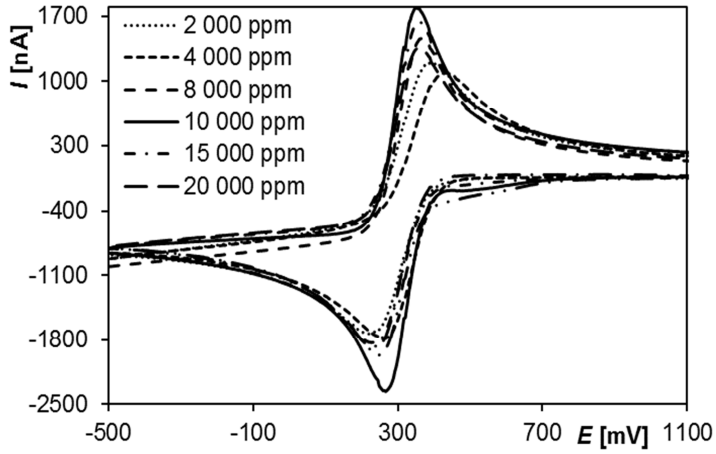

Fig. 1 Cyclic voltammograms of 2.5mM $[Fe(CN)_6]^{3-/4-}$ in 0.1M KCl recorded on BDDEs prepared in media of 2% CH_4/H_2 with the range of B/C from 2 000 to 20 000 ppm; v = 100 mV/s.

Acknowledgement
This work was supported by The University of Pardubice (projects No. SGSFChT_2017_002 and SD373001/82/30350(2016)) and by the grant project of The Czech Science Foundation (project No. 17-03868S).

Properties of screen printed gold electrodes modified with carbon nanomaterials

Natalia Festinger[1], Sylwia Smarzewska[1], Katarzyna Soliwoda[2], Jarosław Grobelny[2] and Witold Ciesielski[1]

[1] *University od Lodz, Faculty of Chemistry, Department of Inorganic and Analytical Chemistry, 12 Tamka Street, 91-403 Lodz*
[2] *University od Lodz, Faculty of Chemistry, Department of Materials Technology and Chemistry, 163 Pomorska Street, 90-236 Lodz*

Taking care of the environment become very popular what leads to constant development of Green Chemistry. According to Principles of Green Chemistry, scientists have been working on miniaturization of chemical equipment to reduce the amount of substances that possess toxicity to human health and the environment. One of the examples for such miniaturization are screen printed electrodes, where working, auxiliary and reference electrode are printed on small ceramic substrate. Screen printed gold electrodes (SPAuEs), used in this research, have been successfully employed as an enzymatic sensors, genosensors and immunosensors.

Examination of electrochemical and electroanalytical properties of graphene oxide modified screen printed gold electrodes (GO-SPAuEs) were carried out using cyclic (CV) and square wave voltammetry (SWV). For this purpose, various volumes of GO suspension in water were dropcasted on the SPAuE surface. The dependence between the dropcasted suspension volume and the electroactive surface of GO-SPAuEs was investigated by cyclic voltammetry technique. The influence of the supporting electrolyte composition on the chosen redox system signals stability and separation was also investigated. Optimized measurement conditions have been applied to the quantitative determination of ascorbic acid (AA). Ascorbic acid signals were much higher on the modified electrode in comparison to signals recorded on the bare electrode. The developed method was used for AA determination in various pharmaceutical formulations. The surface structure of the GO modified screen printed gold electrodes was examined by scanning electron microscopy (SEM).

Comparison of Colorimetric Reagents and Their Applicability in Thermal Lens Spectrometry

Leja Goljat[1], Mikhail A. Proskurnin[2] and Mladen Franko [1]

[1] *University of Nova Gorica, Laboratory for Environmental and Life Sciences, Vipavska 13, POB 301, SI-5001 Nova Gorica, Slovenia*
[2] *Analytical Chemistry Division, Chemistry Department, M.V. Lomonosov Moscow State University, Moscow 119991, Leninskie gory d.1 str. 3, Russia*

Thermal-lens spectrometry (TLS) is an analytical technique, which is characterized by two advantages: high sensitivity amplified by thermophysical parameters of the sample and the ability of measuring chromophore light absorption in a complex[1]. However, TLS is severely hindered by background absorbance, possible photodegradation of analytes, and a limited wavelength set of available laser sources. One of the practical solutions to overcome these disadvantages is the introduction of colorimetric reagents in a specific solvent, which selectively bind the analyte of interest to produce a coloured complex with high absorptivity at the TLS excitation wavelength. In selected solvent, the complex is measured with a thermophysical enhancement of the thermal-lens effect, provided by the thermophysical properties of the solvent. In this study, a potential selective reagent for trace Hg determination, triamterene (2,4,7-triamino-6-phenylpteridine), was investigated from the viewpoint of TLS method development.

Triamterene reacts instantaneously with Hg(II) in a slightly alkaline solution to produce a yellow complex with the absorption maximum at *cca.* 400 nm (dependent on solvent composition)[2]. A TLS spectrometer in a back-synchronized measurement mode, which provides reliable conditions for the measurements of a fully developed (steady state) thermal-lens, was used in this research. Formation ratio, stability constant, and extinction coefficient of Hg(II)-triamterene were studied by UV-Vis spectrophotometry and TLS and compared to those of iron(II) chelate with 1,10-phenathroline as a model system, which was well studied for TLS application previously[3].

The stability constant of the Hg(II)–triamterene complex at selected conditions (H_2O:MeOH (80:20, *v/v)*) was determined by spectrophotometry and TLS to be: $3.82\times10^{10}M^{-2}$ and a 2:1 stoichiometry of Hg(II)-triamterene was found. The average molar absorption coefficient of Hg(II)–triamterene was found to be 5.05×10^{3} $M^{-1}cm^{-1}$, at 415 nm, which shows good agreement of both methods and contradicts the existing literature data[2]. The following solvents were tested: H_2O:MeOH (80:20, *v/v*), H_2O:MeOH (90:10, *v/v*) and H_2O:MeOH (92.5:7.5, *v/v*), and have shown that the solubility of the complex and enchancement of TLS signal favor higher percentage of organic solvents, resulting in signal enhancements of 1.92 and 1.43 for H_2O:MeOH (80:20, *v/v*) and H_2O:MeOH (90:10, *v/v*), respectively, when compared to water. 9.44 times higher slope of the calibration curve in case of Fe(II)-1,10 phenanthroline, together with lower blank signal, results in aprox. 12.7 times lower LOD (in terms of absorbance unites) in comparison with Hg(II)-triamterene.

This research pointed out potential problems, which might derive from inappropriate reagent and/or solvent selection and how some of them can be overcome, to enable highly sensitive TLS determination of nonabsorbing analytes at trace levels.

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Development of the ICP-OES method for determining iodine

Kristýna Bednářová and Anna Krejčová

University of Pardubice, Faculty of Chemical Technology, Studentská 573, 532 10 Pardubice, Czech Republic

Iodine is an essential element and its lack can lead to organism disorders, mostly related to thyroid disease. Iodine can be determined using various methods: chromatographic (IC, HPLC, GC), spectral (ICP-OES, ICP-MS), NAA, electrochemical, and combinations of thereof. The ICP-OES method is a well-established multi-elemental technique and represents a broad linear dynamic range, high analytical sensitivity, however, it is a challenging task for determining non-metals such as chlorine (134.724 nm) and iodine (178.276 nm). At wavelengths below 200 nm, air components (oxygen, water vapor, etc.) are absorbed and therefore, determination of iodine is not sensitive. To overcome this problem, the optical system of the spectrometers is usually filled with an inert gas. A high optical transmission is provided below 125 nm[1].

Iodine substances are used as a contrast medium. Water soluble iodine based contrast agents (ICAs) contain the benzene ring to which three iodine atoms are attached. They diffuse throughout the extracellular space. They are administered directly into the body cavities (the gastrointestinal tract and the urinary tract) and are mainly used in radiography (CT, angiography). These ICAs leave the patient's body unchanged to hospital and municipal wastewaters[2].

The aim of this work was to create a simple ICP-OES method for determination of the total content of iodine in two different types of samples. The first one was a dressing material composed of wheat starch and hyaluronic acid with iodine. The second material was the ICA Iomeron 400, which extracted to hospital waste water is a burden to the environment because of its difficult degradability. The iodine content was determined using the ICP-OES method (Integra XL2, GBC, Australia) at the most sensitive iodine emission line at 178.218 nm. Working conditions were: sample flow rate of 1.5 $ml.min^{-1}$, plasma power 1100 W, the plasma, auxiliary and nebulizer gas flow rates 11, 0.6, and 0.6 $l.min^{-1}$. The calibration standards were 50 - 100 - 200 - 500 $mg.l^{-1}$. The limit of detection is in ICP-OES for I 4.7 $mg.l^{-1}$.

The dressing material contained hyaluronic acid, which can increase a viscosity of sample in solution. In order to precede a high viscosity and a potential losses of iodine, the samples (about 0.1 g) were dissolved in TMAH (6 ml 25%, the final volume 50 ml). The calibration standards were matrix-matched with hyaluronic acid and wheat starch. The dilution factor of original samples was 500, which means the limit of detection of whole procedure 0.05 % of I_2 in the dressing materials. The samples of dressing material theoretically contains 1 - 2 - 4% I_2, which is on the limit of detection capability of the ICP-OES method.

The concentration of iodine coming from the ICM in wastewater is usually 0.5-5 $\mu g.l^{-1}$, in a patient's urine about 5 $g.l^{-1}$. The ICP-OES method is not sufficient for determination of iodine in these samples.

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The *Allium* test – a tool for monitoring the potential health risk of utilizing H_2O_2/UV advanced oxidation processes in drinking water treatment

Mirjana Petronijević[1], Jasmina Agbaba[1], Pavle Mašković[2], Aleksandra Cvetanović[3], Malcolm Watson[1], Aleksandra Tubić[1]and Božo Dalmacija[1]

[1] *Faculty of Sciences, University of Novi Sad, 21000 Novi Sad, Serbia*
[2] *Faculty of Agronomy, University of Kragujevac, 32000 Čačak, Serbia*
[3] *Faculty of Technology, University of Novi Sad, 21000 Novi Sad, Serbia*

In order to secure the microbiological and chemical safety of drinking water, it is necessary to apply different water treatments prior to disinfection. Oxidation processes which involve H_2O_2 in combination with UV irradiation (H_2O_2/UV) are known to be very effective in organic matter and pollutants removal[1]. However, although these water treatments improve the quality of some parameters, they do not guarantee the preparation of healthy and safe water. The applied oxidants may react with other water constituents and potentially form toxic oxidation by-products[2]. It is very difficult to quantify the risk associated with all possible newly formed compounds. Biological tests are therefore an alternative methodology which may be applied to characterise the toxicity of complex samples. The *Allium* test has been recommended as a relatively cheap and rapid toxicity screening test[3] and has been applied for in situ monitoring of the presence of toxic compounds in drinking water[4].

The objective of this research was to examine the impact of H_2O_2/UV advanced oxidation processes on the general toxicity of groundwaters utilizing the *Allium* test. Different groundwaters with various organic matter (2-5 mg C/L) and bromide (0.03-0.05 mg/L) contents were investigated. According to the *Allium* tests, it was concluded that using H_2O_2/UV processes during water treatment resulted in up to 50% increases in water toxicity, depending on the original groundwater investigated. This was reflected in the increased production of bromine-containing organic by-products, including the brominated trihalomethanes, haloacetic acids and haloacetonitriles. In order to reduce the risk of the formation of toxic by-products, it is necessary after the oxidation process to introduce an additional treatment step such as absorption on granulated activated carbon.

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The influence of hormones on water organism and the methods for their determination

Karolina Czarny, Dominik Szczukocki, Barbara Krawczyk, Marek Zieliński, Ewa Miękoś and Karina Kołdziejczyk

University of Lodz, Faculty of Chemistry, Department of Inorganic and Analytical Chemistry, Laboratory of Environmental Threats, 91-403 Lodz, Tamka 12, Poland

In recent years, more and more attention is paid to the introduction of substances into the environment, which can have an adverse effect on the endocrine system of the living organisms. Such compounds are called endocrine disrupting compounds (EDCs). Among them we can find phytoestrogens produced by the plants, substances of anthropogenic origin, such as polycyclic aromatic hydrocarbons (PAHs), pesticides detergents, pharmaceuticals, polychlorinated biphenyls (PCBs), nonyl phenols (NPs), components of plastics (bisphnol A), phthalates or dioxins and natural, as well as synthetic, hormones.

Sex hormones are biologically active compounds and show intensive performance even at very low concentrations (ng/L). The most common environmental hormones are estrogens, which disrupt endocrine processes of organisms living in water reservoirs. They are sufficient enough to have an adverse effect on the endocrine system of organisms living there, to disturb their reproductive processes and their development.

Given the numerous reports on negative effects of exposure of aquatic organisms to the action of estrogens, the development of methods for their determination is becoming more and more popular among the scientists. However, due to the low concentrations of these compounds in the aquatic environment, this is a great challenge. Modern trends in the analytical chemistry require the creation of accurate, sensitive, selective and reliable methods.

Efficient de-agglomeration of polysilane macromolecules in solution and their molecular size

Andraž Mavrič, Artem Badasyan, Mattia Fanetti and Matjaž Valant

Materials Research Laboratory, University of Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia

For application of macromolecules in nanotechnology, where morphology on nanoscale should be precisely controlled, the importance of understanding of a polymer state and its size in a solution is critical. In the case of polysilanes solutions strong inter- and intra-molecular attractions result in agglomeration and successive precipitation even at very low polymer concentrations. This indicates that the conditions are far from theta point (where solvent-solvent, solvent-polymer and polymer-polymer interactions are equal and stable solution is obtained). As a result of insufficient understanding of the polymer state in the solution, determination of molecular weight and size was not accurate[1]. The reported size values for the same polysilane polymer range from about 100 nm to few μm with high discrepancy among techniques. The sources of error can be identified in both the most frequently used measurement techniques, a size-exclusion chromatography (SEC) with a polystyrene standard for a measurement calibration and a light scattering techniques[2].

For three topologically different polysilanes we showed that at room temperature the agglomerates in a size range of 600 - 1300 nm are present. They are precipitating with time. The polysilane solution at room temperature consists of two phases, precipitated particles and particles in solution. With a slight temperature increase to above 40 °C the agglomerates undergo decomposition to the dispersed macromolecules with the size from 15 to 45 nm. The de-agglomeration process was followed with a Dynamic Light Scattering (DLS) and has very similar characteristics for polysilanes of all three different topologies. The decomposition of agglomerates and the transition to a single phase system was studied with an isothermal Differential Scanning Calorimetry (DSC) and a Thermogravimetric Analysis (TGA). In addition, Transmission Electron Microscopy (TEM) was employed to image the individual polysilane macromolecules[3].

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Functionalized high surface area vinylbenzyl chloride polyHIPEs

Doris Golub[1], Mitja Kolar[2] and Peter Krajnc[1]

[1] *University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia*
[2] *University of Ljubljana, Faculty of Chemistry and Chemical Engineering, Večna pot 113, SI-1000 Ljubljana, Slovenia*

Monoliths with high level of porosity and interconnected porous structure can be prepared with wide variety of techniques. PolyHIPEs (polymerized high internal phase emulsions) are porous polymers prepared by polymerizing the continuous phase of an HIPE, wherein the volume of the internal phase is higher than 74 % of the total emulsion volume[1].

Today there are many of methods available to functionalize polyHIPEs, which can be applied in different applications such as chromatography, the separation of heavy metals, chemical synthesis, precursors for supported species and as biocatalyst supports, ion exchange, gas storage devices, tissue engineering and controlled drug delivery[2-4].

L-proline and L-proline derivatives have been successfully used as organocatalysts in several reactions. L-proline acts as a catalyst and radical scavenger and is responsible for enantioselectivity in the studied reactions[5].

Tris(hydroxymethyl)aminomethane (tris or THAM) have been used to scavenge excess electrophiles from solutions. The substitution of a chlorine atom yields an amine derivative with three free hydroxy groups, which are used as scavengers of excess substrates from solution[6].

Polymers functionalized with L-proline and tris(hydroxymethyl)aminomethane can be used as metal chelating polymers that bear specified chemical groups capable of selectively binding materials[7].

The aim of our study was the preparation of poly (4-vinylbenzyl chloride-co-divinylbenzene) polyHIPE monoliths with the interconnected pores functionalized with amines for binding of metals to the polymer from the water systems. PolyHIPE morphology was determined with various procedures – for structural characterization of the monoliths we recorded FT-IR spectra, characterization was also done with elemental analysis and potentiometric titration, porosity and surface area examination was done with Brunauer-Emmett-Teller method.

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Electrochemical sensor based on molecularly imprinted polymer and 3D-ensembles of gold nanowires for L-arabitol detection

Maísa Azevedo Beluomini[1], Nelson Ramos Stradiotto[1] and Paolo Ugo[2]

[1] *Sao Paulo State University (Unesp), Institute of Chemistry, Analytical Chemistry, Department, Rua Professor Francisco Degni, 55, 14800-060, Araraquara, SP, Brazil.*
[2] *Department of Molecular Sciences and Nanosystems, University Ca' Foscari of Venice, Via Torino, 155, 30170, Mestre, Venice, Italy.*

The recent advances in the construction of electrochemical sensors are related to the modification of surface electrodes, which has as its core objective the gaining of sensitivity, selectivity and lower detection limits. In this context, nanotechnology has shown great potential when it comes to the improvement of the performance of these devices. In recent years, three dimensional ensembles of nanowire electrodes (3D-NEEs) have attracted considerable interest owing to their outstanding performance in sensors and electrocatalysis, which is attributed to their special configurations and high surface area. The construction of molecularly imprinted polymers (MIP) immobilized on nanostructures such as 3D-NEEs, has produced patterns of behavior considered different from those obtained on planar electrodes, largely due to the fact that these nanostructures provide increased surface/volume ratio and more locations for imprinting, increasing the capacity of the MIP up to 15 times. In this work we study a new electrochemical sensor, based on 3D-NEEs in order to provide the largest number of accessible locations for the formation of MIPs for the determination of L-arabitol, a residual polyol present in sugarcane vinasse. The 3D-NEEs were prepared using the procedures described previously[1]. The MIP was prepared by electropolymerization of o-phenylenediamine (functional monomer) in the presence of L-arabitol as the template[2]. L-arabitol molecules are trapped in the polymer matrix by hydrogen bonding. After electropolymerization, the electrode was immersed in a mixture of organic solvents with stirring to remove the template of the polymeric matrix, so creating the recognition sites. After template removal, the sensor MIP/3DNEEs can be used for the selective recognition of L-arabitol. The characterization of the sensor was performed by scanning electron microscopy (SEM). Differential pulse voltammograms (DPV) were obtained using 5.0 mM $[Fe(CN)_6]^{3-/4-}$ as the electrochemical probe in which competes with the analyte (non-electroactive) for the binding sites in the cavities. The signal of the probe scaled indeed inversely with the L-arabitol concentration, so allowing the analytical determination of the latter.

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The effects of constant magnetic field on metal electrodeposition

Karina Kołodziejczyk, Marek Zieliński, Ewa Miękoś and Marta Jaksender

University of Łódź, Department of Inorganic and Analytical Chemistry, Laboratory of Environmental Risks, Tamka 12 str., 91-403 Łódź, Poland

The effects of constant magnetic field on electrochemical processes was studied by scientist all over the world. There is area of studies - magnetoelectrochemistry, which deals with those influences. Constant magnetic field may changes parameters of electrodeposition (e.g. deposition time) and morphology, chemical composition and durability of electrodeposited coatings. Metal coatings electrodeposited under constant magnetic field influence may be more durable and their grains may be smaller[1]. The changes in morphology, structure and properties of metals deposited in the presence of constant magnetic field are due to the Lorentz Force, the Paramagnetic Force and the Electrokinetic Force. The Lorentz Force causes the depletion of Nernst diffusion layer and simultaneous creation of Navier-Stokes hydrodynamic layer in the vicinity of the electrode[2].

My presentation concerns the effects of 200 - 1000 mT constant magnetic field on nickel electrodeposition. In our studies nickel was deposited on gold disc electrode under the influence of constant magnetic fields with different values of magnetic induction and different directions of the magnetic induction vector in reference to the working electrode. Nickel was electrodeposited from the solution containing $NiSO_4$. The Saturated calomel electrode was used as reference electrode and the platinum mesh was used as counter electrode. We used methods such as Cyclic Voltammetry, electrodeposition at constant potential and Scanning Tunneling Microscopy in our studies.

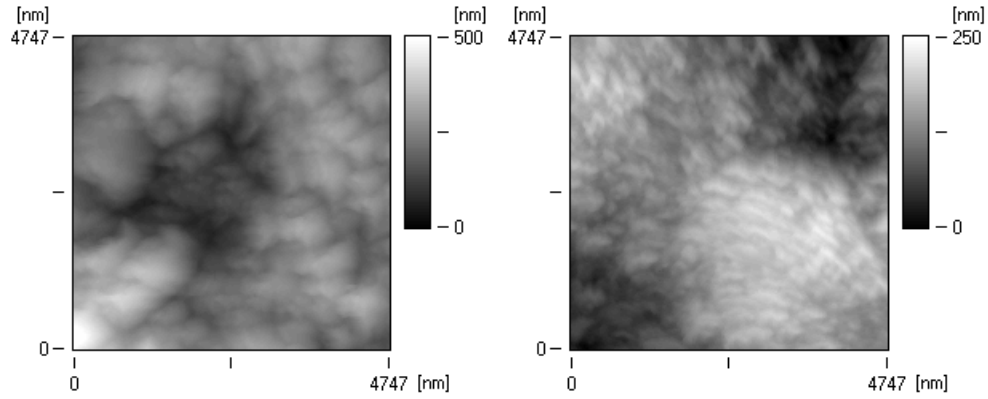

Fig. 1. STM micrographs of nickel electrodeposited on the gold disc electrode in the absence of magnetic field (left) and in the presence of constant magnetic field.

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Preparation and Characterization of Nanoelectrode Ensembles and Disk Microelectrodes

Nicola Ceolotto, M. Antonietta Baldo and Ligia M. Moretto

Department of Molecular Science and Nanosystems, University Ca' Foscari of Venice, Via Torino 155, 30172, Mestre, Venice, Italy

Electroanalytical techniques present many advantages, as for example high sensitivity, low cost, possibility of performing *in situ* measurements, high versatility for application in chemical, biological, food, environment and medical fields.

Moreover, the possibility of miniaturization to produce sensors (makes necessary) requires to enhance the performance of these analytical techniques by developing new materials and new types of electrodes.

In this work, we have characterized and compared the performances of two kinds of gold electrodes, *i.e*. nanoelectrode ensembles (NEEs) and disk microelectrodes (MEs). NEEs are disordered arrays of gold nanodisks (with diameters in the order of nanometers) that have been prepared by electroless deposition on track-etched polycarbonate membranes[1]; MEs are made by single gold disk electrodes, sealed into a capillary of glass, with a electrodic radius in the order of micrometers[2].

NEEs and disk MEs show different mass diffusion mechanisms because of their different dimensions and geometries[3]. The geometric characteristics of the electrodes have been observed by optical and scanning electronic microscopy (SEM).

The electrodes have been characterized by cyclic voltammetry (CV) using as redox probes aqueous solutions of ferrocenylmethyl-trimethylammonium hexafluorophosphate ($FA^+PF_6^-$) in KNO_3 50 mM, and hexamminerutenium(III) chloride ($Ru(NH_3)_6Cl_3$) in KCl 0.1 M. Faradic and capacitive currents have been measured at different scan rate in the potential range 0.1 – 0.8 V by using a potentiostat.

The performances of the electrodes have been examined on the basis of sets of replicated measurements, using $FA^+PF_6^-$ in KNO_3 50 mM as redox probe to make a calibration plot, and by statistical treatments using both the Grubs test to remove the outliers, and test-F to locate the influential points and to see if the variances of each point of the calibration plot of the two electrodes are statistically equivalents[4].

In this communication, the characteristics of these two kinds of electrodes based on the limit of detection, limit of quantification, standard deviation and variances values are presented and compared.

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Advanced nanomaterials and nanoparticles for electroanalytical and SERS application

Maria Sole Zalaffi[1,2] and Paolo Ugo[1]

[1] *Department of Molecular Science and Nanosystems, University Ca' Foscari of Venice, Via Torino 155, 30170, Venezia Mestre, Italy*
[2] *Department of Chemical and Pharmaceutical Sciences, University of Trieste, Via Giorgieri 1, 34127, Trieste, Italy*

The SERS (*Surface Enhanced Raman Spectroscopy*) technique has already been applied in the field of Cultural Heritage to study organic substances using different samples taken from several artistic objects. However, little has been studied about the application on cross-sections mounted on different supports (resins or inorganic salts). This work focuses on the preparation and characterization of nanoparticles (NPs) and nanomaterials suitable for the application of the SERS technique directly on cross-sections of paintings or other works of art. Analyzed organic colorants are anthraquinone-based red lakes and various types of silver and gold NPs can be employed as SERS substrates. In particular, Ag nanostars (AgNSs) are prepared using the one-pot synthesis method which involves the reduction of the metallic precursor ($AgNO_3$) by hydroxylamine in the presence of a capping agent (trisodium citrate) and additives (NaOH)[1]. AgNSs absorb visible light in two spectral regions (550 and 750 nm) thanks to their starry shape composed of a central core and many tips. Due to this a stronger enhancement of the Raman effect (≈10^8) is produced. In principle, an even more intense enhancement could be obtained by using hierarchical structures of nanomaterials (the enhancement factors derived from the attachment of a single Ag nanoparticle onto a gold flat layer were estimated to be as large as 8.3×10^5 [2]). To this aim we are studying the possibility to deposit electrochemically or chemically AgNSs on gold nanowire electrodes (AuNWs) to use them as new SERS substrate. The AuNWs can be obtained by templated synthesis in track-etched polycarbonate membranes[3]. The final objective of this research project is the detection of proteins in artistic materials (e.g. egg tempera[4]) directly on cross-sections using SERS nano-tags bound to the specific antibody for the target protein and to a Raman-probe by means of functional thiols. The nano-tags so bound onto the surface can be mapped using the SERS technique, revealing the distribution of the protein in the cross-section.

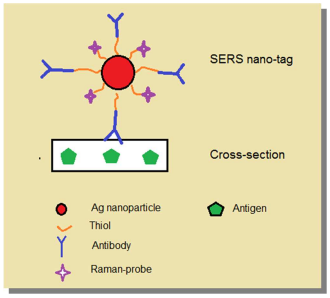

Fig. 1. Scheme representing a SERS nano-tag applied on a cross-section to detect protein materials.

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List of participants

YISAC 2017 - YOUNG INVESTIGATORS

Young investigator	University	Country
Adámková Karolína	University of Pardubice	Czech Republic
Bednářová Kristýna	University of Pardubice	Czech Republic
Beluomini Maísa	Sao Paulo State Univ./ Ca' Foscari Univ. of Venice	Brasil/Italy
Callegaro Alice	Ca' Foscari University of Venice	Italy
Ceolotto Nicola	Ca' Foscari University of Venice	Italy
Czarny Karolina	University of Łódź	Poland
Festinger Natalia	University of Łódź	Poland
Glabonjat Ronald	University of Graz	Austria
Goljat Leja	University of Nova Gorica	Slovenia
Golub Doris	University of Maribor	Slovenia
Gričar Ema	University of Ljubljana	Slovenia
Ivanović Milena	University of Maribor	Slovenia
Kaczmarska Kinga	University of Łódź	Poland
Kašparová Jitka	University of Pardubice	Czech Republic
Kołodziejczyk Karina	University of Łódź	Poland
Kovařová Aneta	University of Pardubice	Czech Republic
Kraševec Ida	University of Ljubljana	Slovenia
Kroepfl Nina	University of Graz	Austria
Krulišová Pavla	University of Pardubice	Czech Republic
Kučerová Simona	University of Pardubice	Czech Republic
Martinková Pavlína	University of Pardubice	Czech Republic
Mavrič Andraž	University of Nova Gorica	Slovenia
Mohorič Urška	University of Ljubljana	Slovenia
Mrzlikar Miha	University of Ljubljana	Slovenia
Ocvirk Miha	Slovenian Institute of Hop Research and Brewing	Slovenia
Padoan Sara	Ca' Foscari University of Venice	Italy
Petronijevic Mirjana	University of Novi Sad	Serbia
Piechocka Justyna	University of Łódź	Poland
Possan André	Univ. Caxias do Sul/ Ca' Foscari Univ. of Venice	Brasil/Italy
Rizzato Giovanni	Ca' Foscari University of Venice	Italy
Robak Justyna	University of Łódź	Poland
Rudnicki Konrad	University of Łódź	Poland
Sipa Karolina	University of Łódź	Poland
Śliwa Julia	AGH-University of Science and Technology	Poland
Štěpánková Michaela	University of Pardubice	Czech Republic
Stiboller Michael	University of Graz	Austria
Surmová Silvie	University of Pardubice	Czech Republic
Tasić Ana	University of Novi Sad	Serbia
Topic Jelena	University of Nova Gorica	Slovenia
Vajdle Olga	University of Novi Sad	Serbia
Węgiel Krystian	AGH-University of Science and Technology	Poland
Žabčíková Simona	University of Pardubice	Czech Republic
Zalaffi Maria Sole	Ca' Foscari University of Venice	Italy
Zanutto P. C. Clariana	São Paulo State Univ./Univ. degli Studi di Pavia	Brasil/Italy
Zupančič Urška	University of Ljubljana	Slovenia

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Supervisor	Institution	Country
Baldo Maria Antonietta	University Ca' Foscari of Venice	Italy
Brycht Mariola	University of Łódź	Poland
Franko Mladen	University of Nova Gorica	Slovenia
Guzsvány Valéria	University of Novi Sad	Serbia
Islamcevic Razborsek Masa	University of Maribor	Slovenia
Kalcher Kurt	University of Graz	Austria
Kolar Mitja	National Institute of Chemistry	Slovenia
Korecká Lucie	University of Pardubice	Czech Republic
Košir Iztok Jože	Slovenian Institute of Hop Research and Brewing	Slovenia
Marolt Gregor	University of Ljubljana	Slovenia
Metelka Radovan	University of Pardubice	Czech Republic
Moretto Ligia Maria	Ca' Foscari University of Venice	Italy
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Skrzypek Sławomira	University of Lodz	Poland
Ugo Paolo	Ca' Foscari University of Venice	Italy
Ventura Karel	University of Pardubice	Czech Republic


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