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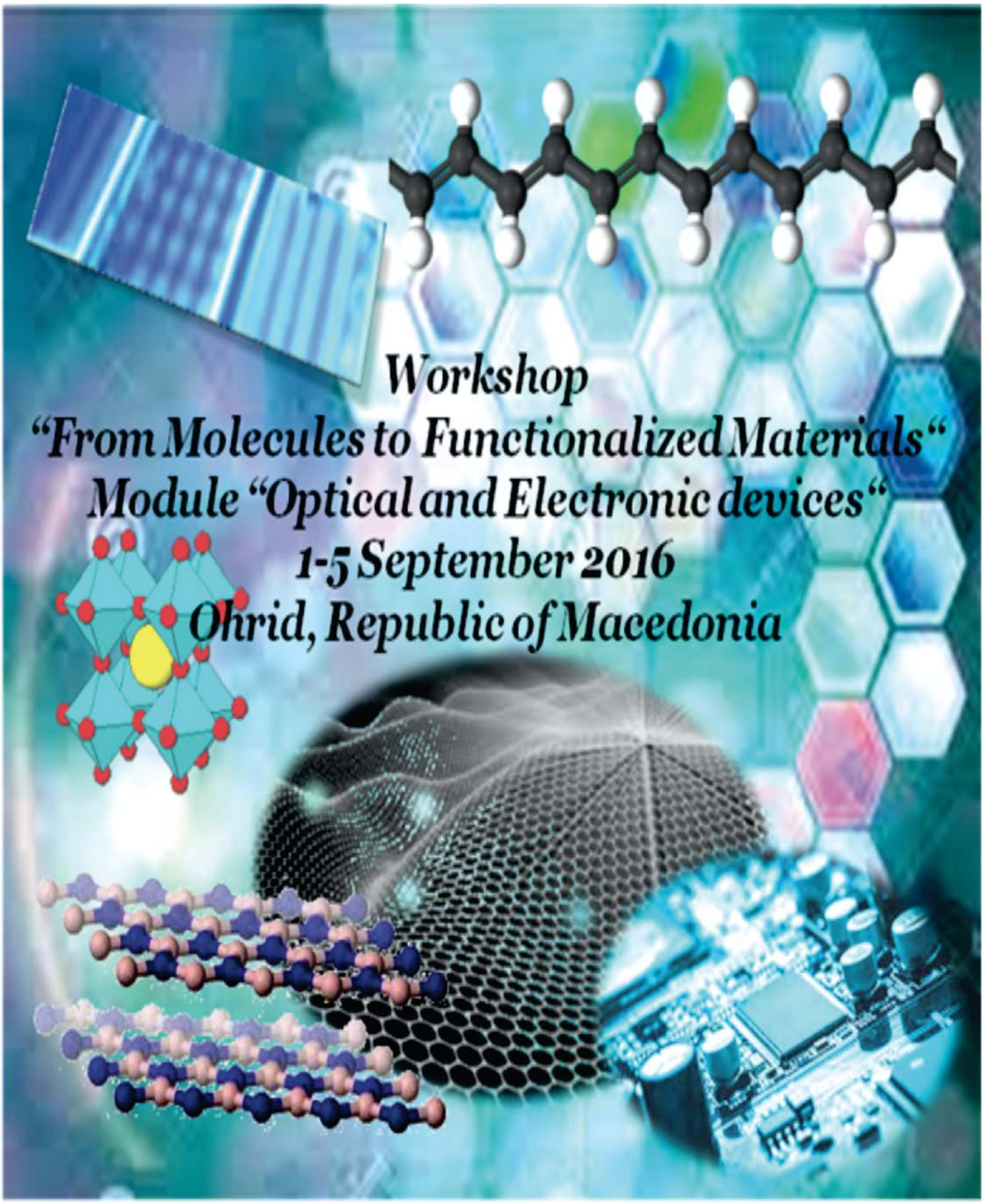

Workshop
“From Molecules to Functionalized Materials“
Module “Optical and Electronic devices“
1-5 September 2016
Ohrid, Republic of Macedonia

INTERNATIONAL MASTER AND POSTGRADUATE
PROGRAMME IN MATERIALS SCIENCE AND CATALYSIS

MatCatNet

Workshop

“From Molecules to Functionalized Materials”

Scientific Module “Optical and Electronic Devices”

PROGRAMME AND ABSTRACT BOOK

1-5-September 2016. Ohrid, Macedonia

PROGRAMME

MatCatNet Workshop
"From Molecules to Functionalised Materials"
and
Scientific module "Optical and Electronic Devices"

1-5 September 2016 Ohrid, Macedonia

Thursday, 1 September 2016

09:00-09:50	**Registration**
09:50-10:00	**Prof. Dr. Evamarie Hey-Hawkins and** **Prof. Dr. Slobotka Aleksovska** ***Welcoming address***

Scientific module
"Optical and Electronic Devices"
-Lectures-

10:00-11:00	**Prof. Dr. Muriel Hissler (Rennes, France)** π-CONJUGATED POLYMERS FOR (OPTO)ELECTRONIC DEVICES
11:00-11:30	*Coffee break*
11:30-12:30	**Prof. Dr. Muriel Hissler (Rennes, France)** π-CONJUGATED POLYMERS FOR (OPTO)ELECTRONIC DEVICES
12:30-14:00	*Lunch*
14:00-14:45	**Assoc. Prof. Dr. Luiza Gaina (Cluj-Napoca, Romania)** PRECURSORS FOR OPTICAL MATERIALS AND DEVICES
14:45-15:30	**Prof. Dr. Slobotka Aleksovska (Skopje, Macedonia)** ORGANIC-INORGANIC PEROVSKITES AS PROSPECTIVE MATERIALS FOR SOLAR CELLS
15:30-16:00	*Coffee break*

16:00-16:45	**Prof. Dr. Metodija Najdoski (Skopje, Macedonia)** ELECTROCHROMISM AND ELECTROCHROMIC DEVICES

Friday, 2 September 2016

09:00-09:45	**Prof. Dr. Fetah Podvorica (Prishtina, Kosovo)** GRAFTING OF ORGANIC FILMS FOR MOLECULAR ELECTRONIC JUNCTIONS
09:45-10:30	**Prof. Dr. Rubin Gulaboski (Štip, Macedonia)** ELECTROCHEMICAL DEVICES - PRINCIPLES AND APPLICATION
10:30-11:00	*Coffee break*
11:00-11:45	**Ass. Prof. Dr. Marjan Randjelović (Niš, Serbia)** COLOR(ED) CENTERS AND RELATED DEFECTS IN CRYSTALLINE MATERIALS FOR OPTO-ELECTRONIC (FUNCTIONALIZED) DEVICES
11:45-12:30	**Dr. Radomir Ljupkovic (Niš, Serbia)** HRTEM AND FESEM IN CHARACTERIZATION OF SELECTED MODERN MATERIALS – PART 1
12:30-14:00	*Lunch*
14:00-14:45	**Dr. Radomir Ljupkovic (Niš, Serbia)** HRTEM AND FESEM IN CHARACTERIZATION OF SELECTED MODERN MATERIALS – PART 2

Minisymposium “Advanced Methods in Chemistry”

14:45-15:15	**Ass. Prof. Dr. Biljana Balabanova (Štip, Macedonia)** OPTICAL EMISSION SPECTROSCOPY: A METHOD FOR CORRELATING EMISSION INTENSITIES TO “REACTIVE PARTICLE DENSITY”
15:15-15:45	**Assoc. Prof. Dr. Violeta Ivanova Petropulos (Štip, Macedonia** BASIC PRINCIPLES OF HIGH PERFORMANCE LIQUID CHROMATOGRAPHY
15:45-16:15	*Coffee break*

16:30- *Sightseeing of Ohrid*

Saturday, 3 September 2016

MatCatNet Workshop
“From Molecules to Functionalised Materials”

-Oral presentations-

Session 1 (Chair: Leon Stojanov)

09:00-09:40 **Muriel Hissler – invited speaker (Rennes, France)**
P-CONTAINING POLYCYCLIC AROMATIC HYDROCARBONS: COORDINATION CHEMISTRY AND OPTO-ELECTRONIC APPLICATIONS

09:40-10:00 *Coffee break*

10:00-10:15 **Éva Andrea Molnár**
(Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca, Romania)

ARYL- AND β-FORMYLATION OF NEW PHENOTHIAZINYL-PORPHYRINS

10:15-10:30 **Arijanit A. Reka**
(Faculty of Natural Science and Mathematics, University in Tetovo, Macedonia)

PHASE TRANSOFRMATIONS OF SILICON DIOXIDE IN DIATOMACEOUS EARTH AT TEMPERATURE RANGE 1000 – 1200 °C

10:30-10:45 **John Popp**
(Faculty of Chemistry and Mineralogy, Leipzig University, Germany)
DENDRITIC FERROCENYL PHOSPHINES FOR REDOX-SWITCHABLE CATALYSIS

10:45-11:00 **Dijana Atanasova**
(Faculty of Medical Sciences, University Goce Delcev– Štip, Macedonia)

OPTIMIZATION AND VERIFICATION OF THE METHOD FOR DETERMINATION OF ANTIOXIDANT ENZYME CATALASE IN VITRO

Session 2 (Chair: Marija Sterjova)

11:00-11:15 **Jeton Halili**
(University of Prishtina, Department of Chemistry, Prishtina, Kosovo)

GC-FID OPTIMIZATION AND VALIDATION FOR SIMULTANEOUS DETERMINATION OF HEROIN IN REAL SAMPLES

11:15-11:30 **Noémi Deak**
(Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca, Romania)

NEW SULFUR-BASED PINCER TYPE LIGANDS:
FROM DESIGN TO APPLICATIONS

11:30-11:45 *Coffee break*

11:45-12:00 **Kaltrina Jusufi**
(University of Prishtina, Department of Chemistry, Prishtina, Kosovo)

DETERMINATION OF HEAVY METALS IN CABBAGE SAMPLES FROM THE AREA SURROUNDING KOSOVO'S POWER PLANTS

12:00-12:15 **Antonio Buzharevski**
(Faculty of Chemistry and Mineralogy, Leipzig University, Germany)

CARBORANYL ANALOGUES OF NONSTEROIDAL ANTI-INFLAMMATORY DRUGS (NSAIDs)

Session 3 (Chair: Patricia Miclea)

12:15-12:30 **Miranda Misini**
(University of Prishtina, Department of Chemistry, Prishtina, Kosovo)

DETERMINATION OF ANTIOXIDANTS WITH ELECTROCHEMICAL BIOSENSORS BASED ON BORON DOPED DIAMOND ELECTRODES AND CARBON PASTE ELECTRODES

12:30-12:45 **Viktorija Maksimova**
(Faculty of Medical Sciences, University Goce Delcev– Štip, Macedonia)

COMPARISON OF OPTICAL AND ELECTROCHEMICAL METHODS FOR DETERMINATION OF THE ANTIOXIDANT EFFECT OF SOME PLANT METABOLITES

12:45-13:00 **Hamdije Memeti**
(Faculty of Natural Science and Mathematics, University in Tetovo, Macedonia)

DETERMINATION OF ADSORPTION CHARACTERISTICS OF NATURAL INORGANIC SORBENTS FOR REMOVAL OF Cr(VI) IONS FROM WATER RESOURCES

13:00-13:15 **Aleksandra Krstić**
(Faculty of Science and Mathematics, University of Niš, Niš, Serbia)

CYCLIC VOLTAMMETRY USING MODIFIED CARBONPASTE ELECTRODES FOR ELECTRO-CATALYTIC ACTIVITY STUDY OF DOPED CARBON MICROSPHERES:
POTENTIAL APPPLICATION FOR ELECTRO-CATALYTIC SENSING

13:15-14:30 *Lunch*

14:30 *Boat trip to St. Naum*

Sunday, 4 September 2016

-Oral presentations-

Session 4 (Chair: Arijanid Reka)

09:00-09:15 **Ionut-Tudor Moraru**
(Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca, Romania)

UNDERSTANDING THE STRUCTURE OF SILOXANIC, GERMOXANIC AND STANNOXANIC SPECIES

09:15-09:30 **Leon Stojanov**
(Faculty of Natural Sciences and Mathematics, Unversity Ss Cyril and Methodius, Skopje, Macedonia)

PREPARATION OF SILVER NANOPARTICLES USING ASCORBIC ACID AND GLUTHATHIONE AS REDUCTIVE REDOX AGENTS

09:30-09:45 **Taulant Demelezi**
(University of Prishtina, Department of Chemistry, Prishtina, Kosovo)

THE EVALUATION OF THE CARBON DIOXIDE SUPERCRITICAL EXTRACTION PERFORMANCE OF VITAMIN C FROM LEMON FRUIT BY THE USE OF ELECTROCHEMICAL METHODS

09:45-10:00 **Sasho Stojkovikj**
(Faculty of Natural Sciences and Mathematics, Unversity Ss Cyril and Methodius, Skopje, Macedonia)

DESIGN OF AMPEROMETRIC SENSORS FOR H_2O_2 BASED ON $K_{0.27}MnO_2 \cdot x\ H_2O$ THIN FILMS

10:00-10:15 **Patricia Miclea**
(Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca, Romania)

ALTERNATIVE PATHS FOR CONTROLLING THE OXIDATION STATE OF CLASS 2 HEMOGLOBIN FROM *ARABIDOPSIS THALIANA*

Session 5 (Chair: John Popp)

10:15-10:30 **Ana Koceva**
(Faculty of Natural Sciences and Mathematics, Unversity Ss Cyril and Methodius, Skopje, Macedonia)

POSSIBILITIES FOR CHEMICAL MODIFICATION AND ANALYSIS WITH INFRARED AND RAMAN SPECTROSCOPY OF GROUND SILICATE GLASS

10:30-10:45 **Angela Trajkovska**
(Faculty of Natural Sciences and Mathematics, Unversity Ss Cyril and Methodius, Skopje, Macedonia)

IR AND RAMAN SPECTROSCOPIC ANALYSIS OF CHEMICALY MODIFIED FLAT SILICATE GLASS

10:45-11:00 **Stefan Jovanov**
(Faculty of Natural Sciences and Mathematics, Unversity Ss Cyril and Methodius, Skopje, Macedonia)

TEMPERATURE-DEPENDENT PROPERTIES OF LIQUID WATER FROM A COMBINED STATISTICAL MECHANICS – NETWORK SCIENCE PERSPECTIVE

11:00-11:15 **Daniela Gjorgjevikj**
(Faculty of Natural Sciences and Mathematics, Unversity Ss Cyril and Methodius, Skopje, Macedonia)

EVALUATION OF THE ELECTROCHEMICAL ACTIVITY OF ASCORBIC ACID AND THE SYNERGY WITH GLUTATHIONE IN DIFFERENT pH ENVIRONMENT

11:15-11:45 *Coffee break*

- Poster flash presentations -

Session 6 (Chair: Aleksandra Krstić)

11:45-11:50 **Marija Sterjova**
(Faculty of Medical Sciences, University Goce Delcev–Štip, Macedonia)

POSSIBILITIES FOR FORMULATION OF TRASTUZUMAB - RADIOIMMUNOGONJUGATES

11:50-11:55 **Elena Drakalska**
(Faculty of Medical Sciences, University Goce Delcev– Štip, Macedonia)

CURCUMIN LOADED HYBRID pH-SENSITIVE LIPOSOMES-PREPARATION AND CHARACTERIZATION

11:55-12:00 **Alexandra-Krisztina Simon**
(Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca, Romania)

SPIN-LABELED BLOOD SUBSTITUTE CANDIDATES: IN VITRO AND IN VIVO EVALUATION

12:00-12:05 **Marija Atanasova**
(Faculty of Medical Sciences, University Goce Delcev– Štip, Macedonia)

VOLATILE COMPOSITION, ANTIOXIDANT AND ANTIMICROBIAL ACTIVITY OF ESSENTIAL OIL FROM *MENTHA ARVENSIS* L. ORGANICALLY PLANTED FROM MACEDONIA

12:05-12:10 **Bojan Bogatinovski**
(Faculty of Natural Sciences and Mathematics, Unversity Ss Cyril and Methodius, Skopje, Macedonia)

DEHALOGENATION OF HEXACHLOROCYCLOHEXANES USING ZINC DUST

12:10–14:00 *Lunch*

Session 7 (Chair: Kaltrina Jusufi)

14:00-14:05 **Dragana Trajkovikj**
(Faculty of Natural Sciences and Mathematics, Unversity Ss Cyril and Methodius, Skopje, Macedonia)

SIMULTANEOUS DETERMINATION OF ACTIVE COMPONENTS IN VETERINARY DRUGS USING UV SPECTROSCOPY AND CHEMOMETRICS

14:05-14:10 **Kire Stojanovski**
(Faculty of Natural Sciences and Mathematics, Unversity Ss Cyril and Methodius, Skopje, Macedonia)

SYNTHESIS AND CRYSTALSTRUCTURE DETERMINATION OF $SmCo_{0.5}Cr_{0.5}O_3$ AND $Sm_{0.8}Ca_{0.2}Co_{0.5}Cr_{0.5}O_{3-\delta}$ PEROVSKITES

14:10-14:15 **Elena Cvetkovska**
(Faculty of Natural Sciences and Mathematics, Unversity Ss Cyril and Methodius, Skopje, Macedonia)

ESTIMATION OF MEASUREMENT UNCERTAINTY FOR ENROFLOXACIN DETERMINATION IN VETERINARY MEDICINAL PRODUCTS BY TWO SPECTROPHOTOMETRIC METHODS

14:15-14:20 **Besart Shatri**
(University of Prishtina, Department of Chemistry, Prishtina, Kosovo)

SYNTHESIS, CHARACTERIZATION AND THE USE OF SUBSTITUTED ARYLDIAZONIUM SALTS FOR THE MODIFICATION OF THE ACTIVATED CARBON POWDER

14:20-14:25 **Elisaveta Nikoloska**
(Faculty of Natural Sciences and Mathematics, Unversity Ss Cyril and Methodius, Skopje, Macedonia)

INFLUENCE OF SILVER SUBSTITUTION ON ELECTROCATALYTIC

PROPERTIES OF $LaCo_{0.5}Fe_{0.5}O_3$ PEROVSKITE

Session 8 (Chair: Noemi Deak)

14:25-14:30	**Alexandra Bogdan** (Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca, Romania) 1,3-DIOXANE DERIVATIVES AS INTERMEDIATES FOR CHEMICALLY AND PHOTOCHEMICALLY ACTIVATED MOLECULAR DEVICES
14:30-14:35	**Fjolla Hashani** (University of Prishtina, Department of Chemistry, Prishtina, Kosovo) THE ROLE OF SURFACTANTS (TRITON X-100 AND SODIUM DODECYLBENZENESULFONATE) ON THE ELECTROCHEMICAL DETERMINATION OF ASCORBIC ACID
14:35-14:40	**Sara Gligoroska** (Faculty of Natural Sciences and Mathematics, Unversity Ss Cyril and Methodius, Skopje, Macedonia) SYNTHESIS AND IDENTIFICATION OF SOME GUANIDINIUM ORGANIC-INORGANIC PEROVSKITES
14:40-14:45	**Ilirijana Osmani** (University of Prishtina, Department of Chemistry, Prishtina, Kosovo) THE ELECTROCHEMICAL MONITORING OF ‘‘EX SITU“ EXTRACTED VITAMIN C
14:45-14:50	**Gjani Hulaj** (University of Prishtina, Department of Chemistry, Prishtina, Kosovo) THE USE OF THE GRAFTED ACTIVATED CARBON POWDERS FOR THE ADSORPTION OF THE LINDANE PESTICIDE FROM MODEL SYSTEMS
14:50–16:30	***Poster session* / *Coffee break***
20:00 -	*Gala dinner*

Monday, 5 September 2016

AN OVERVIEW OF THE MatCatNet PROJECT

09:30-10:00	**Prof. Dr. Evamarie Hey-Hawkins (project leader, Germany)** *An overview of the project: achievements and perspectives*
10:00-10:30	**Prof. Dr. Luminita Silaghi-Dumitrescu** *An Overview of the project – Romanian perspective*
10:30-10:45	**Prof. Dr. Slobotka Aleksovska** *Personal experiences*
10:45-11:15	*Coffee break*
11:00-11:30	***Award ceremony***
11:30-12:30	***Roundtable discussion-*** *Moderator: Prof. Evamarie Hey-Hawkins (project leader)*
12:30-14:30	*Lunch*
14:30-15:30	***Project coordinators meeting***
15:30-16:00	***Closing remarks***
17:00	*Departure*

π-conjugated polymers for (opto)electronic devices

Muriel Hissler

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Over the last twenty years π-conjugated oligomers and polymers have received increasing interest owing to their versatile functions that are demanded for breakthroughs in many interdisciplinary fields like bio-imaging or plastic electronics. For the latter field, organic light emitting diodes (OLEDs) have spearheaded the entry of an entirely new class of semiconductors based on organic molecules into industrial applications. Other devices, such as organic field effect transistors and organic photovoltaic cells, have not yet reached the same marketability, thus motivating substantial research program by academic and industrial groups. The demand for new organic π-conjugated materials with improved electrical and optical properties for plastic electronic applications is still very important and necessitates extensive experimental molecular engineering and theoretical investigations of underlying structure-property relationships.

The first lecture will begin with an introductionon the properties of pi-conjugated systems (p and n doping, modulation and estimation of the HOMO-LUMO gap, estimation of the HOMO and LUMO by different techniques). Then, the second lecture will provide a brief introduction on organic light-emitting diodes, solar cells and field effect transistors.

References:

a) K.MüllenWegner, G. (eds.) *Electronic materials: the oligomer approach*. Wiley-VCH, Weinheim, **1998**.
   J.L. Bredas and S. R. Organic semiconductors (volume 1 and 2)
b) J.Roncali, *Chem Rev.***1997**, *97*, 173
c) Y.J. Cheng, S.-H. Yang, C. S. Hsu *Chem Rev.***2009**, *109*, 5868
d) B. W. D'Andrade, S. R. Forrest, *Adv. Mater.***2004**, *16*, 1585

PRECURSORS FOR OPTICAL MATERIALS AND DEVICES

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The traditional use of organic colorants is to give color to a substrate such as textiles, plastics, paper or leather. In the last years organic colorants have become increasingly important in the electronic applications for the high-technology industries. In electronic applications the organic colorants are often incorporated in a device. The well known applications of functional dyes are OLED, lasers, solar energy conversion, ophthalmic lenses, optical memory and optical displays. This lecture is focused on the synthesis and electronic properties of the functional dyes used for their intrinsic physico-chemical properties.

Key words: Functional dyes, Fluorescence, Photocromism

References:

[1] H. Zollinger, *Color Chemistry, Syntheses, Properties and Applications of Organic Dyes and Pigments*, 3rd Ed. Wiley-VCH, Zurich, Switzerland, 2013.
[2] B. Brem, E. Gal, L. Gaina, C. Cristea**,** A M Gabudean S. Astilean, L. Silaghi-Dumitrescu. Metallo complexes of *meso*-phenothiazinylporphyrins: Synthesis, Linear and nonlinear optical properties *Dyes and Pigments* **2015**, 123, 386-395.
[3] Luiza Gaina, Ioana Torje, Emese Gal, Alexandru Lupan, Cristina Bischin, Radu Silaghi-Dumitrescu, Grigore Damian, Peter Lönnecke, Castelia Cristea, Luminita Silaghi-Dumitrescu, Microwave assisted synthesis, photophysical and redox properties of phenothiazinyl-vinyl-pyridinium dyes, *Dyes and Pigments* **2014**, 102, 1-11.
[4] Emese Gal, Balazs Brem, Iani Pereteanu, Luiza Gaina, Tamas Lovasz, Maria Perde-Schrepler, Laura Silaghi-Dumitrescu, Castelia Cristea, Luminita Silaghi-Dumitrescu. Novel Meso-Phenothiazinyl-Porphyrin Dyes: Synthesis, Optical, Electrochemical Properties and PDT assay. *Dyes and Pigments*, **2013**, 99, 144-153.

ORGANIC-INORGANIC PEROVSKITES AS PROSPECTIVE MATERIALS FOR SOLAR CELLS

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One of the most important aims of current science is the search for clean, renewable and efficient energy sources. In this respect, sunlight is on the very top. Solar energy has many advantages but less disadvantages. One of the huge advantages is its inexhaustible fuel power with minimum detrimental impact on the environment. The technology and devices using solar energy is also versatile. The most promising are solar or photovoltaic cells - devices that convert the energy of light directly into electricity. Their great advantage is the capacity to generate electricity at places that are not linked to an electricity grid. However, the negative aspects that scientists are trying to overcome are the high manufacturing cost and too low efficiencies.

The first generation of solar cells is mainly based on silicon wafers with maximum of 25 % efficiency. The second one includes thin film of amorphous Si, CdTe or copper-indium-galium-selenide (CIGS) grown on different substrates. The third generation, or "emerging photovoltaics", uses variety of new materials including nanotubes, quantum dots, organic dyes (dye-sensitized solar cells, DSSC, or also known as "Grätzel cell"), conductive polymers and perovskite solar cells. In this perspective, solar cells based on semi-conductive organic-inorganic perovskites deposited as a thin film on different substrates (usually TiO_2) are one of the most promising materials that could combine both low cost and high efficiency. The organic-inorganic perovskites can be simply explain by general formula ABX_3, where A denotes organic cation (in most cases methylammonium), B is inorganic cation (Pb or Sn) and X is halogen.

This lecture focuses on development of perovskite solar cells – design, construction, advantages, efficiency, as well as, limitations. The search for new organic-inorganic perovskites suitable for application in photovoltaic devices will be also discussed, particularly the complex perovskites with different metal cations in B-possition, different halides and organic cations with other substituted ammonium cations.

Key words: solar energy, semiconductors, solar cells, organic-inorganic perovskites.

ELECTROCHROMISM AND ELECTROCHROMIC DEVICES

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Electrochromism is the phenomenon of reversible color change or optical density of some materials in the electrochemical system. This kind of materials is well known as electrochromic materials. They have been known since 1968. Electrochromic materials are divided into three classes: Metal oxide thin films, Molecular dyes and Conducting polymers. Metal oxide materials in the form of thin films are subject of extended study. Among these materials are the oxides of cobalt, nickel, vanadium, molybdenum, manganese and tungsten trioxide which the main electrochromic oxide in this class of the electrochromic materials. The thin films of tungsten trioxide exhibit electrochromism with reversible color change from transparent to blue [1]. This phenomenon of reversible color change in the case of electrochromic metal oxides is accompanied with reduction/oxidation processes and reversible ion (most often lithium ions) intercalation/deintercalation.

The electrochromic materials have significant application in electrochromic windows [2] for buildings and aircrafts, electrochromic vehicle mirrors, reflective displays etc. One of the electrochromic applications that has to be emphasized is the dimming windows of Boeing 787 Dreamliner. Most often the electrochromic devices structure consists of two electrochromic thin films deposited on conducting electrodes-substrates separated by an electrolytic layer-ion conductor. These devices work on an external voltage.

Key words: Electrochromism, Electrochromic Devices, Electrochromic Thin Films, Electrochromic Windows, Electrochromic Tungsten Trioxide

References:

[1] P. M. S. Monk, R. J. Mortimer, D. R. Rosseinsky, Electrochromism and electrochromic devices, Cambridge University Press, 139-151, 2007.

[2] R. Baetens, B. P. Jelle, A.Gustavsen, *Solar Energy Materials and Solar Cells*, *94*(2) (2010) 87-105.

GRAFTING OF ORGANIC FILMS FOR MOLECULAR ELECTRONIC JUNCTIONS

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Molecular electronics has known a very rapid growth the last two decades due to its use at wide range in the integrated circuits and to the development of Scanning Probe Microscopy techniques (AFM and STM) as new characterization tools. Organic or inorganic molecules as part of integrated circuits have many advantages among other conventional systems due to their unique electronic properties which may change under potential, light or thermal action. The molecular junction systems (MJS) contain a single molecule or many of them between two conductor (carbon or metal) or semiconductor (silicon) surfaces. The molecule layer thickness is < 10 nm which distinguish them from common organic electronic devices like organic light emitting diodes (OLED), organic field effect-transistors (OFET) with organic film > 100 nm. In MJS the charge transfer mainly is governed by tunnelling and hopping effects. [1]

One of the key elements on MJS is the contact between the molecules and the conductor surface. There exist many methods to attach the organic molecules to solid surfaces. Layer by layer or Langmuir Blodgett and self-assembled thiol monolayers on gold are two techniques that create ordered films but weak interactions with surfaces while covalent chemical and electrochemical grafting of aryl diazonium salts, silanes and Grignard reagents permits strong bonding with metal, carbon, semiconductor and polymer surface. [2] The description of these methods will be the main focus of my lecture.

References:

[1] a) *Nanoelectrochemistry*. M.V. Mirkin and S. Amemiya ed. CRC Press, Taylor&Francis, **2015**; b) McCreery, R.L. *Chem. Mater.*, **2004,** *16*, 4477-4496; c). Xiang, D.; Wang, X.; Jia, C.; Lee, T. and Guo, X. *Chem. Rev.*, **2016**, 116, 4318 – 4440.; d) McCreery, R.L.; Yan, H.; Bergern, A.J. *Phys Chem Chem Phys.*, **2013,** *15*, 1065-1081.

[2] a) *Aryl Diazonium Salts. New Coupling Agents in Polymer and Surface Science*, M. M. Chehimi, ed., Wiley-VCH, Weinheim, **2012**; b) Bélanger, D.; Pinson, J. *Chem. Soc. Rev.* **2011**, *40*, 3995-4048; c) Pinson, J. ; Podvorica F. *Chem. Soc. Rev.* **2005**, *34*, 29-39.

ELECTROCHEMICAL DEVICES - PRINCIPLES AND APPLICATION

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The redox chemistry provides a basis of numerous fundamental physiological and chemical processes. Electrochemical devices are designed to tackle with various redox compounds that are relevant to the occurrence in many natural and artificial systems. We present here the major theoretical principles, the technical design and the applications of some of the most important electrochemical devices. The major focus of this lecture is on the voltammetry as one of the most valuable electrochemical techniques. Hints are given about how to design a voltammetric experiment, the major problems and limitations, as well as the advantages of this technique.

Key words: Electrochemistry, Voltammetry, Instrumentation.

References:

[1] R. Gulaboski, P. Kokoskarova, S. Mitrev, *Electrochim. Acta* **69** (2012) 86-96.

[2] V. Mirceski, R. Gulaboski, M. Lovric, I. Bogeski, R. Kappl. M. Hoth, *Electroanal*. **25** (2013) 2411-2422.

[3] F. Scholz, U. Schroeder, R. Gulaboski, *Electrochemistry of immobilized particles and droplets*, Springer, Berlin, 1-302, 2015.

[4] R. Gulaboski, V. Mirceski, I. Bogeski, M. Hoth, *J. Solid State Electrochem*. **16** (2012) 2315-2328.

[5] V. Mirceski, R. Gulaboski, *Mac. J. Chem. Chem. Eng*. **33** (2014) 1-12.

COLOR(ED) CENTERS AND RELATED DEFECTS IN CRYSTALLINE MATERIALS FOR OPTO-ELECTRONIC (FUNCTIONALIZED) DEVICES

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Color center is a type of crystallographic point defect or point defect clusters associated with trapped electrons/holes that absorbs light in a spectral region in which the crystal itself normally does not absorb light. Color centers can occur naturally in many inorganic crystals and glasses or can be induced by diverse methods (e.g. after exposure of solids to high temperature, high-energy radiation and electrolysis). The term “color center“ was introduced by German scientist Robert Wichard Pohl and it was originally applied to*F*-centers in alkali halides (derived from the German word *Farbenzentren*, or “colorcenters”). The term was related to the special ellectronic configurations in a solid that give rise to optical absorption in a normally transparent spectral region. These fenomena were soon recognized to be of general importance for the understanding of electronic processes in solids.Since these early studies, many different color center types have been characterized and classified in one of two broad categories. One category includes centers with trapped electrons producing *electron excess color centers*. Trapped holes producing *hole excess centers* belong to another category. Solids may contain several different types of color centers, including populations of both electron and holes excess centers in the same (host) matrix. Color centers are usually labeled with a letter symbol. Color centers in crystals can be used to make optically pumped lasers, broadly tunable over various bands in the ultraviolet, the visible, and most importantly, in the 0.8 – 4.0 μm range of the infrared. Moreover, they are promising for realizing quantum devices such as high precision and high resolution magnetic and electric sensors, single-photon sources or quantum memories.

Key words:*F*-centers, opto-electronics, crystal defects, functional materials

References:

[1] L.F. Mollenauer, Color Center Lasers, *Topics Appl. Phys.***59** (1987) 225-277.
[2] J.H. Schulman, Walter Dale Compton, *Color Centers in Solids*, Macmillan, 1962.
[3] R.J.D. Tilley, *Color Centers*, Encyclopedia of Color Science and Technology, 2014.

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HRTEM AND FESEM IN CHARACTERIZATION OF SELECTED MODERN MATERIALS – 1 PART

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Instrumental methods of electron microscopy provide data on the size, morphology and texture of surfaces and particles of materials, as well as on the distribution of particles possibly present on the surface of the metal/metal oxide materials. Three basic electron microscopy methods are: Transmission electron microscopy (TEM), Scanning electron microscopy (SEM) and Scanning Transmission electron microscopy (STEM).

SEM instrumental technique provides information on the morphology of the surface-relief of materials. This method is usually applied during the investigation of materials characterized with primary particles of 100 nm in size or larger particles. Resolution in investigation the two-stage replica of the material is about 2.0 nm.

TEM instrumental technique allows a researcher to register/capture a two-dimensional image of surface and particles of material at the optimal resolution of 0.2 nm. Particles less than 1.0 nm in size can be successively examined using TEM. In the case of investigating larger particles, TEM can be used to obtain data related to the topography of the surface.

By combining the previous two methods, Scanning Transmission electron microscopy (STEM) is obtained. This method can examine the particles smaller than 1.5 nm in size; in the appropriate preset of STEM imaging conditions, the details of the structure of materials can be registered.

HRTEM and FESEM are the most powerful instrumental techniques in the field of electron microscopy, which can record and examine particles smaller than 1.0 nm with high accuracy in*ex situ* as well as *in situ* conditions, which provides significant benefits in testing the advanced modern nano-materials, advanced ceramics with electrical and magnetic properties, piezo-electricity, bioactive ceramics, nano-structured heterogeneous catalysts for a wide variety of industrial applications, as well as adsorbents for environmental protection.

Results on the selected oxides and non-oxides-based materials regarding morphology of the materials would be presented. HRTEM 2D micrograph of the selected locations on the sulfated zirconia-based material to be used as heterogeneous catalyst, and characteristic crystallographic orientations would be shown. The registered dominant crystallographic orientation of zirconia, taking in mind three different orientations at an atomic level is <010> characterized with a presence of so called "short atomic steps". Besides, it is observed a plane orientation {001} that may include Schottky vacancies at the edges. The last two observed crystallographic orientations present potential very active catalytic and/or adsorption sites located at/or near edge of crystallites with high Miller indices. The presence of these sites is closely connected with the expressed favorable initial catalytic activity of the sulfated zirconia-based catalyst in the isomerization of *n*-alkanes [1].

Typical FESEM images of the titania-based thin films deposited onto silicon substrates, obtained by using two different template polymers and two different substrate withdrawal rates during dip-coating procedure by means of evaporation-induced self-assembly method would be presented. The top view of the titania film prepared by using Pluronic F127 polymer as template indicated a complete crack-free surface coverage of substrate. The extensive porosity of the titania film is noticeable, characterized by a narrow pore size distribution, with an average pore size of about 8 nm. Image of the cross-section of this mesoporous titania film revealed a short range, cubic-like ordering of the inter-connected pore structure.

On the contrary, the dip coating process using PSM02 polymer, as a template, leads to the formation of crack-free mesoporous titania films with larger pores (20-22 nm) compared to Pluronic F127 polymer. It is obvious that the use of the polymer with larger molecular mass and consequently larger volume results in the formation of films with larger pore sizes. Image of the cross-section of this mesoporous titania film indicated the elliptical shape of pores and a lower level of their inter-connectivity, which can reduce diffusion of reactants through the film during photo-catalytic reactions of water refining [2].

The samples of spider silk calcite composites were examined by FESEM and used for comparisons of the silks obtained after the first, second, third, fourth and fifth day of bio-mineralization process. FESEM micrographs clearly showed the crystallization of calcite on the spider silk substrate. Thus, FESEM images of the silk surfaces obtained after the first day of bio-mineralization depicts small rhombic crystals with size of 1–3 μm on the spider silk surface.The growth of calcite after the first day was obvious. The micrographs of the samples obtained after the second, third, fourth and fifth day are in coexistence with XRD patterns. The bio-mineralization process promoted the formation of rhombic-shaped calcite crystals. There was no significant difference between the spider silk/calcite composites prepared after immersion within 3, 4 and 5 days except the number and the size of crystals increased with a time of bio-mineralization. The average size of crystals in the spider silk/calcite composites obtained after 3, 4 and 5 days was 6 μm, 9 μm and 11 μm, respectively. Regular form of calcite rhombic crystals with perfect cleavage were homogeneously dispersed trough 3D spider mesh[3].

Photo-luminescent properties of spider silk coated with Eu doped ceria composite can be used as a fluorescent labeling material with modern optical and electrical devices in biomedicine, bioanalysis, drug delivery and bio-scaffolding.

Key words:FESEM, HRTEM, characterization, modern materials, high resolution

References:

[1] A. Zarubica, M. Randjelovic, M. Momcilovic, N. Stojkovic, M. Vasic, N. Radulovic, *Optoelect. Adv. Mater. Rapid Comm.***7** (1-2) (2013) 62-69.

[2]A. Zarubica, M. Vasic, M.D. Antonijevic, M. Randjelovic, M. Momcilovic, J. Krstic, J. Nedeljkovic, *Mater. Res. Bull.***57** (2014) 146-151.

[3] S. Dmitrovic, B. Jokic, M. Prekajski, J. Pantic, D. Zmejkoski, A. Zarubica, B. Matovic, *Proc. Appl. Cer.***10** (1) (2016) 37-40.

HRTEM AND FESEM IN CHARACTERIZATION OF SELECTED MODERN MATERIALS – 2PART

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The electron microscopes present a family of very powerful material characterization techniques. All of them are based on phenomena occurring when accelerated electron-beam interacts with the matter. When the appropriate detection devices are attached to the microscopes, the mentioned phenomena may be analyzed and a lot of information can be obtained. Electron microscopes may provide very useful data about textural, structural, morphological and chemical constitutions of the materials and catalysts. The main advantage of these techniques is a possibility of focusing the electron-beam on very small areas/surfaces of sample, thus, they can be applied at nano-size scale. Electronic microscopy used in one of its many modern variants provides deep insights into the structure of the solid materials. Most applications of the electronic microscopy in catalysis/materials take advantages of high resolution transmission electronic microscopy (HR-TEM) instruments. HR-TEM is one of the most powerful methods/instrumental techniques to direct structural/morphological analysis of the solids. It allows a determination of real-space structures of complex inorganic solids. Field emission microscopy was the first technique capable of imaging surface at a resolution close to atomic dimensions. Field emission microscopy is useful in exploring and understanding the properties of metal surfaces, defects, ordering/disordering phenomena, diffusion of ad atoms and interactions between adsorbed atoms.

Key words: electron microscopy, high resolution, transmission electron microscopy, field emission, scanning electronic microscopy

References:

[1] J.M. Thomas, P.L. Gai,*Adv. Catal.***48** (2004) 171-175.
[2] M. Jose-Yacaman, M. Avalos-Borja, *Catal. Rev. - Sci. Eng.* **34** (1992) 55-61.
[3] A.Y. Datye, D.J. Smith, *Catal. Rev. – Sci. Eng.* **34** (1992) 129-135.
[4]M. Yamada. T. Yoshihara, H. Arima, T. Kobayashi,*J. Electron Microsc.* **46** (1997) 311-317.

OPTICAL EMISSION SPECTROSCOPY: A METHOD FOR CORRELATING EMISSION INTENSITIES TO "*REACTIVE PARTICLE DENSITY*"

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Inductively coupled plasma/optical emission spectrometry (ICP/OES) is a powerful tool for the determination of metals in a variety of different sample matrices. This study gives a general overview of the mentioned analytical technique. With this technique, liquid samples are injected into a radiofrequency (RF)-induced argon plasma using one of a variety of nebulizers or sample introduction techniques. The sample mist reaching the plasma is quickly dried, vaporized, and energized through collision excitation at high temperature. The atomic emission emanating from the plasma is viewed in either a radial or axial configuration, collected with a lens or mirror, and imaged onto the entrance slit of a wavelength selection device. Single element measurements can be performed cost-effectively with a simple monochromator/photomultiplier tube (PMT) combination, and simultaneous multielement determinations are performed for up to 70 elements with the combination of a polychromator and an array detector. The analytical performance of such systems is competitive with most other inorganic analysis techniques, especially with regards to sample throughput and sensitivity.

Key words: ICP-OES, Environmental samples, Optical emission spectrometry

BASIC PRINICPAL OF HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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High-performance liquid chromatography (HPLC) is an analytical technique based on the separation of molecules due to differences in their structure and/or composition. Separation is performed between two phases, mobile and stationary. The molecules in the sample have different affinities and interactions with the stationary support, leading to separation of molecules. Compounds which are longer retained at the stationary phase will elute later, compared to those which are distributed into the mobile phase. Elution of the molecules can be achieved by isocratic or gradient method. In the isocratic method, the composition of the mobile phase remains constant, whereas in the gradient method the composition changes during the separation process. The complexity of the analytical problems requires confirmation of the identity of the peaks through additional qualitative information. This can be achieved by several types of detectors, such as: diode array detector (DAD), fluorescence detector (FLD), refractive index detector (RID) and mass spectrometer (MS). In general, HPLC is used for separation and quantification of polar and non-volatile components.

Key words: HPLC, elution, detection, quantification.

P-CONTAINING POLYCYCLIC AROMATIC HYDROCARBONS: COORDINATION CHEMISTRY AND OPTO-ELECTRONIC APPLICATIONS

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Polycyclic aromatic hydrocarbons (PAHs) are of great potential in molecular materials for opto-electronic devices. Their bandgap and supramolecular organization is tunable through modification of the π-system and lateral aliphatic substituents. An alternative original approach uses the versatility of heterochemistry with the successfull incorporation of N, O, S or B within the π-conjugated framework of PAHs.[1] Here, we report that this strategy can be extended to P-modified PAHs.[2] A synthetic route to a family of P-modified PAHs is described. The reactivity of the P-center allows a straightforward HOMO-LUMO gap tuning. The impact of successive addition of fused aromatic rings around the P-ring was also studied. DFT calculations corroborate these studies. Furthermore, the coordination ability of the P-center allows unprecedented coordination-driven assembly of PAHs onto transition metals. The incorporation of these molecules in White emitting OLEDs shows the potential of this new family of compound for opto-electronic applications.[3]

Key words: Phospholes, PAH, solar cell, OLED

References:

[1] a) S. Draper *et al. J. Am. Chem. Soc.* **2002**, 124, 3486; b) C. Nuckolls*et al. Angew. Chem. Int. Ed.* **2010**, 49, 7909; c) S. Yamaguchi *et al. J. Am. Chem. Soc.* **2012**, 134, 4529.

[2]Bouit, P.-A.; Escande, A.; Szűcs, R.; Szieberth, D.; Lescop, C.; Nyulászi, L.; Hissler, M. ; Réau, R. *J. Am. Chem. Soc.* **2012**, 134, 6524.

[3] F. Riobé, R. Szűcs, P.-A. Bouit, D. Tondelier, B. Geffroy, F. Aparicio, J. Buendía, L. Sánchez, R. Réau, L. Nyulászi, M. Hissler *Chem. Eur. J.* **2015**, 21, 6547.

ARYL- AND β-FORMYLATION OF NEW PHENOTHIAZINYL-PORPHYRINS

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Formyl porphyrins are important intermediates in the construction of more elaborated systems, using several approaches, including the classical reactions of carbaldehyde groups (e.g. Wittig, Grignard, Knoevenagel) [1]. Direct formylation of meso-tetraarylporphyrins are commonly achieved by the Vilsmeier reaction, which allows mono- and di-formylated compounds only at the β-pyrrolic positions.

In our case two different methods were investigated to obtain the target formyl-porphyrins: Vilsmeier-Haack reaction [2] and lithium-halogen exchange [3].

The Vilsmeier-Haack reaction is carried out by using acid-resistant metalloporphyrins (Cu, Ni, Pd) with excess of formylating agent. The regioselective bromine-lithium exchanges of *meso*-bromo-substituted porphyrin were achieved. Direct lithiation of free-base bromo-arylporphyrins and subsequent formylation with DMF gave various formyl-porphyrin derivatives in excellent yield.

The structures of obtained compounds were investigated by spectroscopic methods (NMR and HRMS measurements) and the optical properties were studied using UV-Vis spectroscopy.

Key words:formyl porphyrin, Vilsmeier-Haack reaction, bromine-lithium exchange

References:
[1] A. Balakumar, K. Muthukumaran, J. S. Lindsey, *J. Org. Chem.*, **2004**, 69, 5112-5115.
[2] N. M. M. Moura, M. A. F. Faustino, M .G. P. M. S. Neves, A .C. Duarte, J.A.S. Cavaleiro, *J. PorphyrinsPhtalocyanines*, **2011**, 5, 652-658
[3] E. Onal, V. Ashen, J. Pecaut, D. Luneau, C. Hirel, *Tetrahedron Lett.*,**2015**, 56, 5157-5160.

PHASE TRANSOFRMATIONS OF SILICON DIOXIDE IN DIATOMACEOUS EARTH AT TEMPERATURE RANGE 1000 – 1200 °C

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The phase transformations of silicion dioxide has a very important role in the applicationof diatomaceous earth in the production of ceramic products. Therefore the phase transformations are observedwith the use of DTA and TGA at temperatures up to 1100°C, and diatomaceous earth in powder state heated at temperature1000–1200°C for a period of 1 and 2 hours. DTA and TGA analyzis show that during thermal treatment up to 1100°Cthe diatomaceous earth remains in its amorphous phase. Roentgen-structural examinations of probes heated at 1000–1200°C fora period of 1–2 hours show no presence of crystalline phases at 1100°C. XRD examinations of probes heated at1200°C show presence of the crystalline phases cristobalite and quartz. The samples was heated at 1200°C for a periodof 2 hours, and was observed with an increase of the cristobalite content compared with quartz. SEM and TEMexaminations results of diatomaceous earth heated at 1200°C for a period of 2 hours show that the probes undergoes sinteringfollowed by reduced porosity.

Key words:diatomaceous earth, thermal treatment, phase transformations, sintering

References:

[1] D. Lack, First-order amorphous-amorphous transformationin Silica, The American Physical Society, Physical Review Letters, Volume 84 No 20, p-p. 4629–4632 (2000).

[2] Bogoevski, S., Jančev, S., Boškovski, B.- Characterizationof Diatomaceous Earth from Slavishko Pole localityin the Republic of Macedonia, Geologica Macedonica,Vol. 28, No. 1, 39–43 (2014).

[3] Reka, Arianit A., Anovski, Todor, Bogoevski, Slobodan,Pavlovski, Blagoj, Boškovski, Boško: Physical-chemicaland mineralogical-petrographic examinations of diatomitefrom deposit near village of Rožden, Republic of Macedonia,GeologicaMacedonica, Vol. 28, No. 2, pp. 121–126 (2014).

DENDRITIC FERROCENYL PHOSPHINES FOR REDOX-SWITCHABLE CATALYSIS

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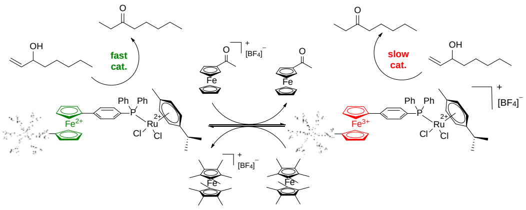
In recent catalyst development, the attention turned to homogeneous catalysts whose activity in different chemical processes can be switched by an external stimulus. Recently, our group reported on the redox control of a catalytic process, which also corroborates the power of dendritic structures in homogeneous catalysis.[1] By adding a chemical oxidant or reductant, it was possible to reversibly switch the catalytic activity of the dendritic ferrocenyl phosphine ruthenium(II) complexes.



To employ this ligand system also for homogeneous asymmetric transformations, we have focused on implementing a stereogenic phosphine responsible for asymmetric induction within the ligand. By way of JUGÉ’s ephedrine-based method[2], *P*-stereogenic ferrocenyl phosphines were synthesized, which were successfully grafted onto the first and second generation phosphorus-containing dendrimers from the research group of CAMINADE.[3]Consequently, we have obtained *P*-stereogenic dendritic ferrocenyl phosphine ligands which will now be applied in asymmetric and homogeneous transition metal catalysis.

Key words:dendrimers, ferrocene, redox-switchable catalysis, *P*-stereogenic phosphines

References:

[1] P. Neumann, H. Dib, A.-M. Caminade, E. Hey-Hawkins, *Angew. Chem., Int. Ed.* **127**(2015),316–319.

[2] S. Jugé, M. Stephan, J. A. Laffitte, J. P. Genet, *Tetrahedron Lett.* **31**(1990), 6357–6360.

[3] N. Launay, A.-M. Caminade, J. P. Majoral, *J. Organomet. Chem.* **529**(1997), 51–58

OPTIMIZATION AND VERIFICATION OF THE METHOD FOR DETERMINATION OF ANTIOXIDANT ENZYME CATALASE IN VITRO

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The human body constantly controls the presence of pro-oxidants and antioxidants. The balance between them is closely regulated and is very important for keeping the vital cell functions. The cell is permanently exposed to attacks from different external and internal forms on reactive oxygen species. [1]The hydrogen peroxide is a compound from the biosphere and it is one of the most common reactive oxygen species. On the other side, an antioxidant enzyme catalase is well studied because of its important function in cell protection from the potentially toxic effects of hydrogen peroxide.[2]Therefore, the aim of our study was to determine the activity of erythrocyte catalase in hemolysate using modified and optimized UV spectrophotometric method of Aebi (1984). The method monitors the rate of decomposition of the substrate - hydrogen peroxide (H_2O_2) at a wavelength of 240 nm. The method was optimized in order to achieve the optimal sample dilution and optimal time point for measuring the decrease in the absorbance due to the substrate decomposition. The data obtained showed that the sample should be diluted 1:1000 to achieve the activity of catalase in the range of 0.01 KU/ml – 0.04 KU/ml. As we obtained the best correlation factor when measuring the decomposition of hydrogen peroxide 30 s after the initiation of the reaction (R2 = 0.995), we chose to measure the change in absorbance in two time points, immediately and 30 s after addition of the substrate in the reaction mixture. The performance verification of the method was assessed through the determination of the parameters linearity and reproducibility. The results proved that the method is linear in the concentration range of 0.01 KU/ml – 0.04 KU/ml. The t-test showed that the method is reproducible (there is no statistically significant difference in the results obtained in two consecutive days of measurement, p = 0,1643). With this optimized method we determined the erythrocyte catalase activity in hemolysate of 23 healthy volunteers. The blood samples were collected in the Department of Occupational Medicine in the Institute of Public Health of R. Macedonia.

Key words: catalase, acatalasemia, hydrogen peroxide, method verification, method optimization

References:

[1] Giordano CR, Roberts R, Krentz KA, Bissig D, Talreja D, Kumar A, Terlecky SR, Berkowitz BA. Catalase therapy corrects oxidative stress-induced pathophysiology in incipient diabetic retinopathy. Invest Ophthalmol Vis Sci. 2015 May

GC-FID OPTIMIZATION AND VALIDATION FOR SIMULTANEOUS DETERMINATION OF HEROIN IN REAL SAMPLES

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Heroin (diacetylmorphine) is a synthesized opioid analgesic, which is found naturally in the opium poppy. The analytical analysis of these drugs is of a great importance for ensuring the limited use, illegal smuggling and the abuse of these drugs. Heroin is a common drug of abuse with potentially harmful and unpleasant effects to the health. The determination of these molecules in real samples it's a difficult task, due to the matrix interference. In order to quantify various other cutting agents in addition to alkaloids, a gas chromatographic (GC) method was developed to facilitate simultaneous quantification of heroin and target analytes commonly found in illicit heroin seized in Kosovo. The validation results demonstrated high selectivity. The linearity of the method for heroin was determined as (0.05-1.00 mg/ml). Correlation coefficients of linearity were found between (0.9946-0.9992). Based on the selectivity/sensitivity there is no interferences and method considered very selective. Defining the limit of detection (LOD's), is found by comparing of the signal/noise ratio. LOD's and LOQ value for heroine is found to be 25 ng respectively 0.25µg. Based on the signal/noise ratio, is proved that capillary column HP50 (semipolar) is more sensitive than DB1 capillary column (nonpolar). Based on the results obtained in quantitative analysis for heroin can be noticed that in case samples, the content of heroin varies from 2.25% to 59.05%. Case samples, besides heroin, also contain other ingredients such as (Codeine, Caffeine, Acetaminophen,Tetramisole, Lidocaine).

Key words: Heroin, Gas chromatography, LOD's, LOQ.

References:

[1]. Kneisel, S., & Auwärter, V. (2012). Analysis of 30 synthetic cannabinoids in serum by liquid chromatography-electrospray ionization tandem mass spectrometry after liquid-liquid extraction. *Journal of mass spectrometry*,*47*(7), 825-835.
[2]. De Castro, A.; Concheiro, M.; Shakleya, D.M.; Huestis, M.A. Simultaneous quantification of methadone, cocaine, opiates, and metabolites in human placenta by liquid chromatography-mass spectrometry. J. Anal. Toxicol. 2009, 33, 243–252.
[3]. Dams, R., Murphy, C.M., Lambert, W.E. and Huestis, M.A., 2003. Urine drug testing for opioids, cocaine, and metabolites by direct injection liquid chromatography/tandem mass spectrometry. *Rapid communications in mass spectrometry*, *17*(14), pp.1665-1670.

NEW SULFUR-BASED PINCER TYPE LIGANDS: FROM DESIGN TO APPLICATIONS

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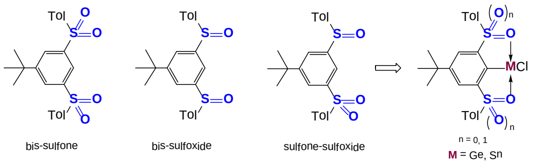
Pincer ligands are mainly used in the chemistry of transition metals due to the particular characteristics. They have as a main feature the ease to modify their properties by adjusting the structure (the ligand backbone and its substituents, the donor groups).[1] For this reason, lately the role of these ligands in the stabilization of heavy p-block elements also came in focus. There are several examples of compounds based on pincer type ligands, among which metallylenes (heavier analogues of carbene) too, containing amine, imine, ether or phosphonate moieties as donor groups.[2] In the last years in our research group a new family of pincer type ligands was designed, containing sulfonyl or sulfinyl moieties as donor groups, in order to test the capability in obtaining metallylenes (Scheme 1).



Scheme 1

The complete characterization of the pincer ligands is in progress, as well as the evaluation of their capacity to stabilize low valent p-block elements. The first studies were realized on the bis-sulfone ligand (n = 1), where a germylene and a stannylene have been obtained and their coordination ability was tested. [3,4] The studies continue on the other two ligands.

Key words:pincer ligand, germylene, stannylene

References:
[1] G. van Koten, *Top. Organomet. Chem*., **2013**, 40, 1-20.
[2] R. Jambor, L. Dostál, *Top.Organomet. Chem*., **2013**, 40, 175-202.
[3] M. El Ezzi,R. Lenk, D. Madec, J. M. Sotiropoulos, S. Mallet-Ladeira,A. Castel, *Angew. Chem. Int. Ed*., **2015**, 54, 805 –808.
[4] N. Deak, P. M. Petrar, S. Mallet-Ladeira, L. Silaghi-Dumitrescu, G. Nemeş, D. Madec, *Chem. Eur. J.* **2016**, *22*, 1349-1354.

DETERMINATION OF HEAVY METALS IN CABBAGE SAMPLES FROM THE AREA SURROUNDING KOSOVO'S POWER PLANTS

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Heavy metals are defined as metallic elements that have a relatively high density compared to water [1]. Numerous industrial activities contribute with the pollution of heavy metals directly or indirectly in soil through the releases of solid wastes, waste gases, and wastewater [2]. Now it is a known fact that pollution with heavy metal is a major concern, this particularly of the case when it penetrates freely in the food chain.

To determine the actual pollution in cabbage, we collected thirty samples of soil and cabbages and analyzed the heavy metal pollution. The cabbage samples were analyzed in washed and unwashed form to identify the impact of dust pollution.

The treatment of cabbage samples where digested in microwave system, in the presence of HNO_3 and H_2O_2.To do the determination of heavy metal content, we used ICP-AES technique.

From the results obtained, we can conclude that the concentrations of heavy metals are high in some regions in the vicinity of Kosovo power plants.

Keywords: heavy metals, plants, pollution, ICP-AES technique.

References:

[1] Fergusson JE, editor. The Heavy Elements: Chemistry, Environmental Impact and Health Effects. Oxford: Pergamon Press; 1990.

[2] Bradl H, editor. Heavy Metals in the Environment: Origin, Interaction and Remediation Volume 6. London: Academic Press; 2002

CARBORANYL ANALOGUES OF NONSTEROIDAL ANTI-INFLAMMATORY DRUGS (NSAIDs)

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A highly coveted approach in the design of novel nonsteroidal anti-inflammatory drugs (NSAIDs) is achieving cyclooxygenase-2 (COX-2) selectivity. This approach, however, is lately associated with increased risk of heart diseases [1]. A useful strategy to circumvent this is the implementation of NO-releasingmoieties in the target structure.Furthermore, it has been shown that the implementation of the carboranyl moiety, as a phenyl mimetic, in biologically active molecules results in compounds that can exhibit improved biological stability and activity in comparison to their generic paradigms [2].

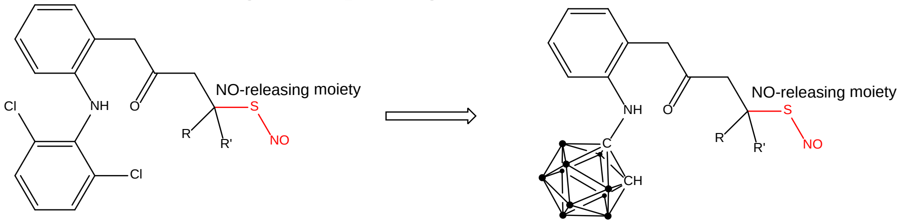

Fig. 1 Proposed structure of the carboranyl analogue of diclofenac with an NO-releasing moiety

Our work focuses on the implementation of the carboranyl moiety in the structures of known COX inhibitors. The substitution of the phenyl moiety with a carborane unit is expected to yield more selective COX-2 inhibitors that are more robust and show greater resistance to catabolic transformations within the body. Furthermore, the NO-containing prodrugs are expected to have a better heart safety profile.

Key words:carboranes, NSAIDs, drug design

References:

[1] K.D. Rainsford, *Anti-Inflammatory Drugs in the 21st Century*, in *Inflammation in the Pathogenesis of Chronic Diseases*, R. Harris et al. (editors), 2007, Springer Netherlands, p. 3-27.

[2] M. Scholz, E. Hey-Hawkins, *Carbaboranes as Pharmacophores: Properties, Synthesis, and Application Strategies.Chem. Rev.*, **2011**, *111*, 7035-7062.

DETERMINATION OF ANTIOXIDANTS WITH ELECTROCHEMICAL BIOSENSORS BASED ON BORON DOPED DIAMOND ELECTRODES AND CARBON PASTE ELECTRODES

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Antioxidants are closely involved in the prevention of cell damage and widely used as ingredients in dietary supplements in the hope of maintaining health and preventing diseases such as cancer and coronary heart disease. Boron-doped diamond electrodes were investigated for their ability to detect phenolic antioxidants whereas electrochemical behavior was compared to carbon paste electrodes. The purpose of this research was to develop a simple and inexpensive analytical procedure for the electrochemical quantization of hydroquinone as analyte. The studies were made with cyclic voltammetry technique for characterization and hydrodynamic amperometry for quantifications. During this study BDDEs and CPEs were modified with gold nanoparticles (AuNPs) and carbon nanotubes (CNTs inactive and activated).

From the results obtain, it may be concluded that BDD is a very good electrode material for the determination of phenolic compounds at positive potentials; whereas carbon paste is in some cases comparable but shows strong adsorption.

Keywords: Antioxidants; Cyclic voltammetry; Hydrodynamic amperometry;Boron-doped diamond electrode; Carbon paste electrode.

COMPARISON OF OPTICAL AND ELECTROCHEMICAL METHODS FOR DETERMINATION OF THE ANTIOXIDANT EFFECT OF SOME PLANT METABOLITES

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Since plant metabolites became very popular as natural antioxidants, there are many *in vitro* assays reporting their antioxidant activity. Spectroscopic assays are most frequently used in the literature, but there are few novel electrochemical methods established recently.

In this study we compared the antioxidant activity of few phenolic compounds measured by electrochemical method versus their antioxidative potential measured by spectroscopic method, using ascorbic acid as a referent substance. The antioxidative potential of vitamin E, quercetin, capsaicin and dihydrocapsaicin, was examined by means of cyclic voltammetry directly on the surface of a glassy carbon electrode. These results were compared with the results obtained for the same compounds by the spectroscopic FRAP method. It has been shown that the antioxidant potential of these substances obtained by the method of cyclic voltammetry was few times higher compared to their potential measured for the same concentrations by the spectroscopic method, when using the ascorbic acid as reference. It could be suggested that this significant difference is due to the different pH of the medium used in both assays.

These results lead to a conclusion that because of some disadvantages of the spectroscopic assays (incubation time and pH of the medium), the electrochemical methods could became more suitable for this purpose. In addition, the antioxidative role of the plant metabolites commonly ingested through nutrition is important in physiological conditions or pH of the medium close to neutral, which are not prescribed in the FRAP protocol, or other spectroscopic methods.

Key words: cyclic voltammetry, FRAP, phenolic compounds, spectroscopy.

DETERMINATION OF ADSORPTION CHARACTERISTICS OF NATURAL INORGANIC SORBENTS FOR REMOVAL OF Cr(VI) IONS FROM WATER RESOURCES

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The heavy metals pollution is a serious environmental problem, especially the presence of the hexavalent chromium ions in the water resources. The removal of Cr(VI) from wastewaters is a necessitybecause of its toxicity for the living beeings and the environment. In this research we focused on the new ways of removal of Cr(VI) ions from aqueous solutions using natural inorganic materials. For this aim we selected five natural minerals from different micro-localities in the Republic of Macedonia: aksil (KrivaPalanka), trepel (Bitola), SiO_2 amorphous (Kozuf), pemza (Bojanciste) and bentonite (KrivaPalanka). With aim to find low cost and highly efficient adsorbents for elimination of Cr(VI) ions from industrial wastewater, complete characterization of natural mineral materials was done. Physical, chemical and mineralogical examinations were performed for each of investigated material. The following experimental techniques were used to characterize the adsorbents: XRD, TGA-DTA and FT-IR. In order to determine the amount of the adsorbed hexavalent chromium ions UV/VIS and AAS were applied. The adsorption experiment were performed at constant room temperature, different initial Cr(VI) ions concentrations and at different pH of the solution. The equilibrium data were analyzed by Langmuir isotherm and maximal adsorption capacity was determined. The surface area of the sorbents were measured by BET method. With aim to the dermine the optimum pH value for maximal removal of Cr(VI) ions, the point of zero charge, pH_{PZC}, for investigated materials wereobtained.

Key words: natural inorganic materials, Cr(VI), adsorption, point of zero charge, equilibrium

References:
[1] D. Biswajit, K. M. Naba, R. Palas and Ch. Soumya, *Chem.Sci Trans.*,**2** (2013), 85-104.
[2] V. Swarnakar, N. Agrawal and R. Tomar, Sorption of Chromate by HDTMA-Exchanged Zeolites, *J. Chem. Pharm. Res.*, 3 (2011), 520-529.

A CYCLIC VOLTAMMETRY USING A MODIFIED CARBONPASTE ELECTRODES FOR ELECTRO-CATALYTIC ACTIVITY STUDY OF DOPED CARBON MICROSPHERES: POTENTIAL APPPLICATION FOR ELECTRO-CATALYTIC SENSING

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Modified carbon paste electrode, based on paraffin oil as a binder, has been applied for the characterization of Ag- and Pt-doped carbon microspheres as electro-catalysts using cyclic voltammetry of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ under various experimental conditions. Bare and doped carbon microspheres (CMS) were fabricated by using the hydrothermal method and used for carbon paste electrode modification. The characteristics of CMS were investigated using SEM and FTIR techniques. CMS ranging from 0.5 to 8 μm in average, as evidenced by SEM, showed slight influence of dopant nature onto their microstructure. FTIR analysis revealed that the involvement of metal species in the carbon structure was followed by their subsequent reduction and rising of oxidized carbon functionalities in the spectra. Electrochemical study showed that all the examined electrodes performed reversible processes with chemically stable generated products and no side chemical reactions. Among the electro-catalysts investigated, Pt-doped carbon microspheres*displayed the best* electro-catalytic performance in terms of heterogeneous transfer rate constant and other kinetic parameters. Since minimal addition of Pt in the hydrothermal synthesis resulted in powerful electro-catalytic effect as precious advantage, benevolent impact of carbon microspheres as catalyst support was put into focus of this research.

Key words:carbon microspheres,cyclic voltammetry, modified carbon paste electrode, electro-catalytic application

References:

[1] Y. Mi, W. Hu, Y. Dan, Y. Liu,*Mater. Lett.***62** (2008) 1194–1196.
[2] I. Taurino, S. Carrara, M. Giorcelli, A. Tagliaferro, G. De Micheli, *Surf. Sci.***606** (2012) 156–160.
[3] J. Zhang, Y. Zhang, S. Lian, Y. Liu, Z. Kang, S.-T. Lee, *J. Coll. Inter. Sci.***361** (2011) 503–508.

UNDERSTANDING THE STRUCTURE OF SILOXANIC, GERMOXANIC AND STANNOXANIC SPECIES

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Silicon-based polymers, widely used in our daily life, are obtained by the polycondensation of small siloxanic molecules. Similar to siloxanes, germoxanes and stannoxanes represent also the cornerstone in the synthetic procedures of new materials being also used as precursors in catalysis. By comparison to ethers, silo-, germo- and stannoxanic species exhibit particular structural features, namely large E-O-E bonding angles (E = Si, Ge, Sn) and on the other hand, short E-O bond lengths, significantly shorter than the sum of the covalent radii of their constituent atoms.

Recent papers published by Weinhold and West [1, 2] rationalize the particular behavior of the Si-O-Si moieties as a consequence of vicinal hyperconjugative interactions, overcoming other theoretical models such as the p→d back-bonding or the ionic one.

Our main goal for this study was to assess the structural behavior of Ge-O-Ge and Sn-O-Sn moieties in terms of hyperconjugative effects, similar to the ones exposed for siloxanic units. For these purposes, model compounds (Scheme 1) were investigated through DFT calculations, used in conjunction with NBO techniques, in order to emphasize the importance of specific electronic effects.

Scheme 1.

Key words:siloxanes, germoxanes, stannoxanes, hyperconjugation, DFT, NBO

References:
[1] F. Weinhold, R. West, Organomet. 30 (2011) 5815-5824.

[2] F. Weinhold, R. West, J. Am. Chem. Soc. 135 (2013) 5762-5767.

PREPARATION OF SILVER NANOPARTICLES USING ASCORBIC ACID AND GLUTHATHIONE AS REDUCTIVE REDOX AGENTS

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Silver nanoparticles have been formed by reduction of Ag^+ ions from $AgNO_3$ aqueous solution by using reductive redox agents such as ascorbic acid and gluthathione in an ammonium acetate/acetic acid buffer at pH 5.3. The preparation has been conducted by mixing equimolar solutions of reactants at concentration of 10^{-4} mol/dm^3. Formation of colloidal solutions containing silver nanoparticles has been confirmed by electrochemical, spectroscopic and microscopic techniques. The declining of the concentration of the free Ag^+ ions following the reduction with the reductants has been measured by anodic stripping voltammetry using square-wave voltammetry as a potential modulation form. By applying UV-VIS spectroscopy the formation of nanoparticles has been supported with the specific surface plasmon resonance absorption peak at 350 nm. Finally, the morphology and dimensions of the formed silver nanoparticles have been studied by inspecting microphotographs collected by atomic force microscopy. Considering morphology, uniformity and dimensions of the formed nanoparticles the best results have been obtained by applying glutathione as a reductive agent, most likely due to its ability for both complexation and reduction, as well as due to the slow kinetics of the redox reaction.

Keywords: Silver nanoparticles, SWV, UV-Vis spectrometry, AFM, ammonium acetate/acetic acid

THE EVALUATION OF THE CARBON DIOXIDE SUPERCRITICAL EXTRACTION PERFORMANCE OF VITAMIN C FROM LEMON FRUIT BY THE USE OF ELECTROCHEMICAL METHODS

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Ascorbic acid (AA) is a water-soluble vitamin that is found in numerous biological systems and fresh fruits or vegetables. AA plays a significant role in different biochemical processes (immune response activation, iron absorption, is involved in wound healing, powerful antioxidant which fights against free-radical induced diseases, etc.).

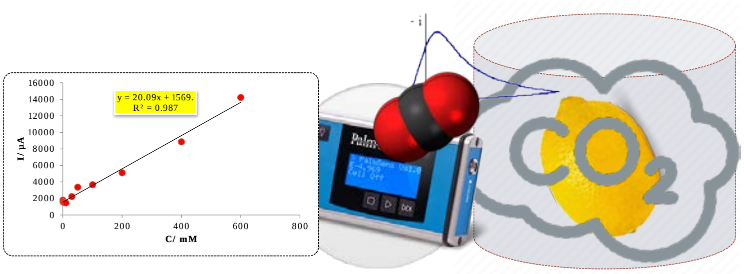

Figure 1. Calibration curve for the ‘’Ex situ’’ electrochemical determination of AA molecule onto Pt electrode by using cyclic voltammetry.

Among different extraction techniques, supercritical extraction with carbon dioxide (SC-CO_2) represents a very powerful green extraction technique that avoids the use of toxic solvents making it very appealing to our study for the extraction of vitamin C from lemon fruit. Although there are a numerous analytical methods for determination of this molecule, due to its electrochemical behavior this molecule can be easily and cost effectively determined by electrochemical methods such as cyclic voltammetry. The electrochemical determination of the ascorbic acid was performed in the aqueous media after its extraction by SC-CO_2 by evaluating the height of its oxidation wave and comparing the electrochemical signal with that of the calibration curve (Figure 1). The determination of the AA was done ‘’ex situ’’ after its extraction. The future work is oriented toward the ‘’in situ’’ electrochemical determination of this molecule the SC-CO_2 on Pt electrodes by using Cyclic Voltammetry (CV) and Differential Pulse Polarography (DPP).

Key words: ascorbic acid, supercritical extraction, cyclic voltammetry.

DESIGN OF AMPEROMETRIC SENSORS FOR H_2O_2 BASED ON $K_{0.27}MnO_2{\cdot}xH_2O$ THIN FILMS

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The scientific interest in the development of electrochemical sensors for hydrogen peroxide based on transition element substances, especially manganese compounds modified electrodes is very attractive nowadays. We have designed a new kind of simple and cheap nonenzymatic amperometric sensor based on $K_{0.27}MnO_2{\cdot}xH_2O$ modified FTO electrode for detection and quantification of hydrogen peroxide. A thin film of $K_{0.27}MnO_2{\cdot}xH_2O$ is deposited on the FTO surface using simple chemical deposition method. The chemical composition and structure of the deposited material are studied using XRD and FTIR spectroscopy. The electrochemical and sensing properties are studied using cyclic voltammetry and chronoamperometry. All electrochemical measurements are carried out in three electrode system using phosphate buffer solution ($HPO_4^{2-}/H_2PO_4^-$) with pH = 7.5 as electrolyte in the presence of atmospheric oxygen. The best results are obtained at potential of +0.30 V in concentration range of H_2O_2 from 1 up to 20 μM. The calibration plot is associated with a linear amperometric response and coefficient of $R^2 = 0.99$.

Key words: H_2O_2, $K_{0.27}MnO_2{\cdot}xH_2O$, nonenzymatic sensors, chronoamperometry

References:
[1] W. Chen, S. Cai, Q. -Q. Ren, W. Wen, Y. -D. Zhao, *Analyst* **137** (2012) 49-58.

[2] M. Asif, A. Aziz, A. Q. Dao, A. Hakeem, H. Wang, S. Dong, G. Zhang, F. Xiao, H. Liu, *Anal. Chim. Acta* **898** (2015) 34-41.

[3] S. Dong, J. Xi, J. Wu, H. Liu, C. Fu, H. Liu, F. Xia, *Anal. Chim. Acta* **853** (2015) 200-206.

[4] M. Najdoski, V. Koleva, S. Demiri, S. Stojkovikj, *Mater. Res. Bull.* **47** (2012) 2239-2244.

ALTERNATIVE PATHS FOR CONTROLLING THE OXIDATION STATE OF CLASS 2 HEMOGLOBIN FROM *ARABIDOPSIS THALIANA*

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In the early 1990s non-symbiotic plant hemoglobins (nsHbs) were discovered and latter studies classified them into three classes[1]. *Arabidopsis thaliana* contains nsHb's from each class. Glb2 is found in the rosette leaves and its overexpression is triggered by hypoxia[2].

Hemoglobins can undergo autoxidation generating the toxic radical superoxide O_2^- and methemoglobin (Fe^{3+}) - which can no longer bind O_2. The *in vivo* mechanisms controlling the oxidation state of plant globins are still unknown, but fundamental in view of the remarkable differences between nsHbs oxidation states and the heme's ease in shifting between them

This study evaluates Glb2 autoxidation rates and provides some insights into its mechanism, while searching for a proper way to slow it down - using different natural antioxidants like ascorbate, glutathione and NADH. From this approach, the interaction between Glb2 and human blood was also investigated.

Key words:autoxidation, non-symbiotic, hemoglobin, Arabidopsis thaliana, reduction

References:

[1] Garrocho-Villegas V, Gopalasubramaniam SK, Arredondo-Peter R., Plant hemoglobins: what we know six decades after their discovery. *Gene*,***2007***, 398,78-85.

[2] Dordas C, Rivoal J, Hill RD., Plant Haemoglobins, Nitric Oxide and Hypoxic Stress.,*ANN Bot*.,***2003***, 91,1089-1096.

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POSSIBILITIES FOR CHEMICAL MODIFICATION AND ANALYSIS WITH INFRARED AND RAMAN SPECTROSCOPY OF GROUND SILICATE GLASS

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Samples of powdered silicate glass were treated employing different reagents and different conditions [1-3] in order to activate the surface of the glass particles and enrich its surface with hydroxyl groups. The processes of surface activation and modification were studied using vibrational spectroscopy techniques like Fourier Transform Infrared Attenuated Total Reflection (FTIR-ATR), Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFT) and Raman spectroscopy. The results show a possible activation through the appearance of a weak band at 3749 cm^{-1} in the ATR spectra due to the free OH groups. The DRIFT spectra on the other hand show a complex broad band below 3690 cm^{-1} which is probably due to the hydrogen bonded water and OH groups in the structure of the glass. One of the activated powdered glass samples (when using "piranha solution" for activation purposes) was further treated with 3-aminopropyltrimetoxysilan (APTMS) with intention to further modify the surface of the powdered silicate glass through chemisorption. The whole process was carried out in a Schlenk line (in a N_2 atmosphere). The DRIFT and Raman spectra showed a presence of APTMS on the glass surface through the appearance of $\nu(CH_2)$ bands. In order to specify whether APTMS is chemisorbed or physisorbed, an extraction with diethyl ether on a modified glass power was performed. Raman spectra revealed that APTMS is mostly physisorbed.

Keywords: Silicate glass, FTIR-ATR, DRIFT, Raman spectroscopy, APTMS

References:

[1] L. Xiao, X. Zheng, T. Zhao, L. Sun, F. Liu, G. Gao, A. Dong Colloid Polym. Sci. 291 (2013) 2359–2364.
[2] E. Metwalli, D. Haines, O. Becker, S. Conzone, C.G. Pantano, J. Colloid Interface Sci 298 (2006) 825–831.
[3] J.A. Howarter, J.P. Youngblood, Langmuir 22 (2006) 11142–11147

IR AND RAMAN SPECTROSCOPIC ANALYSIS OF CHEMICALY MODIFIED FLAT SILICATE GLASS

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Soda-lime silicate glass is a widely used material and a starting material for a wide range of glass products [1,2]. The bonding of 3-Aminopropyltrimethoxysilane (APTMS) on silica gel or glass has been reported in many publications [3,4] and the spectroscopic analysis provides information indicating a possibility for chemical modification of the glass surface. Hydrolysis of the Si-O bonds (where O is a bridging oxygen) and formation of silanol (Si-OH) groups on the glass surface can be used to increase the reactivity of the surface. This reactivity can then be used in many procedures for further modification of the glass as a cheap and available material. The activation of the glass surface was done by hydroxylation using three different procedures that included acid and alkaline hydrolysis of the siloxy groups and formation of silanol groups on the surface of the glass. The product of activation was analyzed using ATR-FTIR spectroscopy where a successful hydroxylation would give a band originating from the OH stretching vibration in the region of 3800-3700 cm^{-1}. Further modification of the so activated glass was made employing 3-aminopropiltrimetoxysilane in inert conditions. The proof of successful modification was obtained using FTIR and Raman spectroscopy where a band of CH_2 stretching vibration absorbing in the 2950-2850 cm^{-1} wavenumber region indicated presence of APTMS molecules on the glass surface.

Key words: Silicate glass, Modification, 3-aminopropyltrimethoxysilane, Infrared spectroscopy, Raman spectroscopy.

References:
[1] M. Jacoby, *Chem. Eng. News* **90** (2012) 34–36.
[2] M. N. Tahir, D. Jeong, H. Kim, J Yu, E. Cho, and S. Jung, *Bull. Korean Chem. Soc.* **35** (2014) 39–44.
[3] E. Metwalli, D. Haines, O. Becker, S. Conzone, C.G. Pantano, *J. Colloid Interface Sci.* **298** (2006) 825–831.
[4] M. Bukleski, V. Ivanovski, *Maced. J. Chem. Chem. Eng.* **33** (2014) 267–275.

TEMPERATURE-DEPENDENT PROPERTIES OF LIQUID WATER FROM A COMBINED STATISTICAL MECHANICS – NETWORK SCIENCE PERSPECTIVE

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The non-covalent intermolecular interactions of hydrogen-bonding type in liquid water were analyzed from the viewpoint of graph theory in the context of science of complex networks. Monte Carlo simulations of liquid water in the *NPT* ensemble were carried out at several temperatures, spanning the range from 4 to 80 °C. The MC-derived configurations were analyzed from structural and energetic aspects so that the presence of intermolecular hydrogen bonding between pairs of water molecules could be unequivocally determined. Subsequent to determining geometrical and energetic parameters to quantify the very existence of intermolecular hydrogen bonding, the network of noncovalently interacting molecules has been converted into a non-directed, non-weighted complex network by means of graph-theoretical approach. Various static parameters characterizing the complex network properties (such as e.g. degree and degree distribution, network neighborhood analysis etc.) were derived as a function of temperature of the "realistic" medium. At the same time, a random network (random graph) was generated under the same conditions with respect to the "realistic" graphs obtained from MC simulations of water and its analogous properties were determined as well. An attempt was made to related the properties of liquid water at various temperatures, viewed as a complex network of noncovalently interacting molecular species, to the properties of an analogous random graph.

Key words: liquid water, hydrogen bonding, Monte Carlo simulations, network science, graph theory

EVALUATION OF THE ELECTROCHEMICAL ACTIVITY OF ASCORBIC ACID AND THE SYNERGY WITH GLUTATHIONE IN DIFFERENT pH ENVIRONMENT

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The formation and activity of a number of chemical compounds, known as ROS (reactive oxygen species), which have a tendency to donate oxygen to other substances, causes potentially harmful effects on organisms. Free radicals and antioxidants are terms that are used more commonly every day [1]. The purpose of this experimental study was to examine the electrochemical activity of ascorbic acid and the synergistic effect of glutathione and ascorbic acid at various pH values.

In the body, ascorbic acid (AscH2) and glutathione (GSH) represent strong reducing agents and by reducing the many substances that cause oxidative stress, they have antioxidant properties.

The survey was conducted by applying square-wave voltammetry (SWV) using black graphite electrode as a working electrode. The great sensitivity of this technique enabled us insight into the effects that ascorbic acid and glutathione have individually, and with each other, by changing the frequency of the signal and the concentration of the tested compounds. The experiments were performed at three different pH environments (pH = 2,pH = 7 and pH = 9), in order to see the influence pH has on the activity of these compounds.

Key words: Ascorbic acid, glutathione, square-wave voltammetry, synergistic effect

References:

[1] V. Lobo, A. Patil, A. Phatak, N. Chandra, Free radicals, antioxidants and functional foods: Impact on human health, *Pharmacogn Rev*, **Vol.4(8)** (2010): 118–126A.

POSSIBILITIES FOR FORMULATION OF TRASTUZUMAB - RADIOIMMUNOGONJUGATES

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Trastuzumab (Herceptin®) is a commercially approved humanized IgG1 monoclonal antibody for treatment of HER2 positive breast cancer. Monoclonal antibodies are selective and specific anticancer therapy which are used for conjugation with another dugs, toxins and radioisotopes. In recent years, with the development of radiopharmacy, are synthesized many stable conjugates with various bifunctional chelators (DOTA, DTPA, HYNIC, 1B4M-DTPA, TCMC), for further labeling with radioisotopes.

In order to increase the selectivity of the drugs and toxins and the good clinical results of trastuzumab encouraged many scientists to try to formulate stable conjugates.All radioimmunoconjugates of trastuzumab are in phase of preclinical and clinical examination and allows significant improvement in the general conditions of the patients. For imaging and identification of HER2 positive lesions are developed immunoconjugates labeled with γ and β^+emitters (^{99m}Tc-HYNIC-trastuzumab,^{111}In-DOTA-trastuzumab, ^{64}Ga-DOTA-trastuzumab,^{68}Ga-DOTA-trastuzumab). *In vitro* and *in vivo* investigations shows thatconjugates labeled with pure β and α emitters are new promising drugs in treatment of HER2 postitive cancers which allows selective uptake of radioimmunoconjugates by the tumor cells and minimal localizaton in healthy organs. Till now,^{177}Lu-DOTA-trastuzumab, ^{90}Y-DTPA-trastuzumab, ^{212}Pb-TCMC-trastuzumab, ^{227}Th-DOTA-*p*-benzyl-trastuzumab and ^{225}Ac-trastuzumab, given good *in vivo* results and selective internalization in HER2 positive breast, prostate and ovarian cancer cells.

The goal of this examinationis to formulate stable freeze dried kit trastuzumab-conjugate with bifunctional chelators (DOTA, DTPA, HYNIC and 1B4M-DTPA) and *in vitro* chemical characterization and identification. The most stable conjugate will be used for obtaining radioimmunogonjugates with ^{68}Ga and ^{177}Lu and their preclinical in vitro and in vivo biodistribution using animal models.

Key words: Trastuzumab, breast cancer, immunoconjugates, radioispotopes, bifunctional chelators.

CURCUMIN LOADED HYBRID pH-SENSITIVE LIPOSOMES-PREPARATION AND CHARACTERIZATION

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Curcumin, the yellow powder derived from the plant Curcuma Longa, exhibited numerous therapeutic applications against wide range of chronic diseases such as diabetes, pancreatitis, arthritis, neurodegenerative diseases and various types of cancer without toxicity to normal cells. Despite the numerous advantages, clinical realization of curcumin‘s potential has been limited due to its poor aqueous solubility (11ng/ml) and very low systemic bioavailability. An intriguing strategy to overcome these limitations is the design of nanosized drug delivery systems. Present study reports the preparation and characterization of hybrid pH-sensitive liposomal nanoparticles as platforms for delivery of curcumin. The pH-sensitive liposomes based on dipalmitoylphosphathydilcholine:cholesterol (DPPC:CHOL) and a pH-sensitive poly(isoprene-b-acrylic acid) (pI-pAA) were prepared by lipid film hydration method and extrusion, whereby curcumin is entrapped as a free drug and as a water soluble inclusion complex with polyoxyethylated calix[4]arene.Physicochemical characteristics of the nanoparticles (size, size distribution and zeta potential) were evaluated by DLS and the results revealed particles of app.180 nm with monomodal distribution (PDI below 0.2) and zeta potential of – 20 mV suitable for systemic application. Hybrid pH-sensitive liposomes showed significantly improved drug release profile. Formulated curcumin also presented superior cytotoxic activity in comparison with the free drug.

These findings give us a reason to conclude thatthe hybrid pH-sensitive liposomal nanoparticles are promising platforms for curcumin.

Key words:curcumin, nanoparticles, liposomes, polyoxyethylatedcalix[4]arene, DLS

SPIN-LABELED BLOOD SUBSTITUTES CANDIDATES: IN VITRO AND IN VIVO EVALUATION

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Two hemoglobin (Hb) based blood substitutes were selected and investigated using EPR spectroscopy combined with site-directed spin labeling (SDSL), a method widely used for investigating the dynamics and structure of the proteins. The spin labeling procedure[1] entails the specific addition of the spin label of choice to a site at the two native β93 cysteines residues in the hemoglobin tetramer.

The candidates, copolymerized Hb with albumins[2], both human serum albumin (HSA) and bovine serum albumin (BSA), were tested *in vitro* by exposing them to living cells, *Escherichia coli* cultures and human umbilical vein endothelial cells (HUVEC). Also, *in vivo* tests on animals were performed which provided information about the lifetime of the copolymer into the circulatory system, and the undergone structural changes.

Key words:hemoglobin, blood substitutes, site-directed spin labeling, EPR spectroscopy

References:
[1] Klare JP, Steinhoff HJ, Spin Labeling EPR, *Photosynthesis Research*, **2009**, 102, 377-390.

[2] Scurtu F, Zolog O, Silaghi-Dumitrescu R, Hemoglobin-Albumin Cross-linking with Disuccinimidyl Suberate (DSS) and/or Glutaraldehyde for Blood Substitutes, *Artificial Cells Blood Substititutes and Immobilization Biotechnology*, **2014**, 42, 13-7.

VOLATILE COMPOSITION, ANTIOXIDANT AND ANTIMICROBIAL ACTIVITY OF ESSENTIAL OIL FROM *MENTHA ARVENSIS* L. ORGANICALLY PLANTED FROM MACEDONIA

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The volatile composition, antioxidant and antimicrobial activity of essential oils from flowers, leaves and whole plant of *Mentha Arvensis L.* organically planed from the territory of Macedonia were object of this study. The essential oils from dried and powdered plant materials were isolated by hydro-distillation using Clevenger-type apparatus.[51,51] The composition of three essential oils was identified by GC-MS and quantified by GC-FID. [51,51] Fifty-five components were identified and quantified in the three essential oils isolated from the flowers, leaves and whole Mentha plant. The most abundant component in all three oils was menthol with 35.64%, 32.47% and 52.53% respectively. The second most dominant component in the three essential oils was isomenthone with 20.38%, 15.97% and 8.42% respectively. All other components were in quantity less than 8%. The antioxidant activity of essential oil from whole Mentha plant was determined against ABTS radical with value of 1.58 TE mg/L of oil. The antimicrobial activity of essential oil isolated from whole Mentha plant was determined against Escherichia coli and Candida albicans. Our results showed significant antibacterial activity against Escherichia coli ATCC 25922 (24 mm) and significant antifungal activity against Candida albicans ATCC 10231 (32 mm).

Key words: Mentha arvensis plant, essential oil, volatile composition, antioxidant activity, antimicrobial activity.

References:

[1] Tiwari, Recent advances and callenges in trichome research and essential oil biosynthesis in *Mentha arvensis L.*, *Ind. Crop. Prod.* **82** (2016) 141-148.

[2] B. R. Rajeswara Rao, Biomass and essential oil yields of cormint (*Mentha arvensis* L. f. *piperascens* Malinvaud ex *Holmes*) planted in different months in semi-arid tropical climate, *Ind. Crop. Prod.* **10** (1999) 107-113.

DEHALOGENATION OF HEXACHLOROCYCLOHEXANES USING ZINC DUST

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Hexachlorocyclohexanes (HCHs) and their main representative lindane (γ-hexachlorocyclohexane) were produced in Macedonia by the factory OHIS for a period of around a decade from the mid 1960^{ies} to mid 1970^{ies}. After those few years of "fame" lindane fell to complete notoriety. There are two main landfill sites in the circle of the factory with over 30,000 tones of chemical waste of different HCH isomers. There are several existing methods for dehalogenation of HCHs of which several are based on zero-valent metals[1]. A successful method for dechlorination and partial reuse of the HCHs was developed.

The dehalogenation process on the mixture of HCH isomers obtained from one of the landfill sites was based on direct metal mediated approach using zero-valent zinc dust. The mixture of HCHs were dissolved in methanol at room temperature and afterwards zinc dust was added, followed by few drops of glacial acetic acid for the activation of zinc. The reaction temperature was 65 °C for a period of 10 hours. The dehalogenation was monitored by simple developed GC-MS headspace method where the amount of the obtained benzene was monitored. Another way of monitoring the reaction progress was by utilizing IR spectroscopy. After the given reaction time the resulting mixture was worked-up and the GC-MS analysis showed no presence of HCHs (*i.e.* complete dechlorination). The products of the dechlorination of HCHs were benzene and zinc chloride ($ZnCl_2$). The obtained mixture of methanol and benzene can be distilled off and reused in dechlorination of a new batch of HCHs by-products. The activation of zinc and the use of hydroxylic solvent, such as methanol, were necessary for successful dechlorination.

Key words: Hexachlorocyclohexanes (HCHs), dechlorination, zinc dust, GC-MS.

References:

[1] S. Suresh, *Reductive Remediation of Pollutants Using Metals*, The Open Waste Manag. J. **2** (2009), 6-16.

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SIMULTANEOUS DETERMINATION OF ACTIVE COMPONENTS IN VETERINARY DRUGS USING UV SPECTROSCOPY AND CHEMOMETRICS

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Veterinary drugs represent a special class of antibiotics that provide a good treatment of animals infection. Inadequate doses may cause some side effects that impair animal's health. [1] In fact, animal health care has reached an impressive degree of comparability to human's health care. Therefore, besides the great significance to monitor the drug use continuously, it is equally important to control the active components content in the drugs.

UV/Vis spectroscopy was used for simultaneous determination of sulfadimidine (SDM), neomycin (NMC) and oxytetracycline (OTC) in veterinary drug formulation Neosulfox-P. The analysis was performed using Varian Cary 50 UV-Visible Spectrophotometer, in a 1 cm quartz cell, at range 190 – 400 nm, with 0.5 nm resolution and 300 nm/min scan rate. The modeling was performed using counter-propagation artificial neural networks (CPANN). For this purpose a total number of 91 samples were prepared according to a properly preselected experimental design. 64 of these samples were used as a training set, while the remaining 27 samples were used as a test set for external validation of the final models. The selection of the wavelengths most suitable for modeling purposes as well as the selection of the CPANN [2] training parameters, was performed with the use of genetic algorithm (GA). Using this approach the best performances and the simples models were obtained for OTC. Due to the low absorption coefficient of NMC band in UV/Vis spectrum, the performances of the initial models used for prediction of NMC were the lowest. However, with the help of GA, for this active compound, we obtained models which have comparable prediction performances to the other two substances. The final results for simultaneous determination of these active compounds show that coefficient of correlation for the test set, in the best models obtained using GA, vary between 0.997 and 0.999.

Key words: veterinary drugs; UV/Vis spectroscopy; chemometrics; CPANN; genetic algorithm;

References:

[1] Jim Fingleton; *Legislation for veterinary drugs control;* Fao legal papers; pp. 1-14; Italy, 2004.
[2] J. Zupan, J. Gasteiger; *Neural Networks in Chemistry and Drug Design*; pp. 30-33; Weinheim, 1999.

SYNTHESIS AND CRYSTALSTRUCTURE DETERMINATION OF $SmCo_{0.5}Cr_{0.5}O_3$ AND $Sm_{0.8}Ca_{0.2}Co_{0.5}Cr_{0.5}O_{3-\delta}$ PEROVSKITES

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The synthesis, crystal structure determination and calculation of crystallochemical parameters of $SmCo_{0.5}Cr_{0.5}O_3$ and $Sm_{0.8}Ca_{0.2}Co_{0.5}Cr_{0.5}O_{3-\delta}$ perovskites are presented. The perovskites were synthesized by solution combustion method using glycine as a fuel. The obtained perovskites were analyzed by powder X-Ray Diffraction (XRD). The XRD patterns showed that these perovskites are isomorphous. The crystal structures, refined by the Rietveld method, showed that these perovskites crystallize in ortorhombically distorted perovskite structures, within the space group *Pnma* ($Z = 4$).

Contrary to expectations, the unit cell volume of $Sm_{0.8}Ca_{0.2}Co_{0.5}Cr_{0.5}O_{3-\delta}$ is smaller in comparison with $SmCo_{0.5}Cr_{0.5}O_3$, probably because of the stronger binding affinity of Ca to oxygen compared to Sm. The main reason for the deviation of the ideal perovskite structure is the octahedral tilting, which is evident in both of the perovskites, but in the $Sm_{0.8}Ca_{0.2}Co_{0.5}Cr_{0.5}O_3$ perovskite it is also noticeable a distortion of the BO_6 octahedrons.

The lattice parameters and distances and angles were used to calculate several crystallographic parameters such as, cell distortion, orthorhombic distortion, bond and angle deformation, the tilting angles, bondvalences, and global instability index. The crystallochemical calculations were used to obtain a clearer picture of the influence of substitution of Sm^{3+} with Ca^{2+} in these complex perovskites on the distortion and stability of the perovskite structure.

Keywords: perovskites, XRD, Rietveld method, crystal structure, crystallochemical calculations.

ESTIMATION OF MEASUREMENT UNCERTAINTY FOR ENROFLOXACIN DETERMINATION IN VETERINARY MEDICINAL PRODUCTS BY TWO SPECTROPHOTOMETRIC METHODS

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The uncertainty in measurement is an inevitable part for the estimation of chemical analytical results, and the results without an uncertainty estimate cannot be considered as complete [1]. The aim of this work was estimation of combined standard and extended measurement uncertainty (MU) for two simple and rapid UV-VIS spectrophotometric methods for assay determination of enrofloxacin in veterinary drug formulations Enroxil Flavour 50 mg tablets and Enroxil 5% injection solution. The first one was based on absorbance measurement of enrofloxacin in 0.01 M NaOH at 271 nm, while the second method was based on yellow coloured complex formation between enrofloxacin and Fe(III) ion, exhibiting λ_{max} at 431 nm. The approach applied for the MU estimation was according to the Guide for the expression of uncertainty in measurement [2].

The MU estimation was performed for three different concentration levels for both methods. From the reproducibility data, it could be concluded that the second method was the more precise one (lower input of the type A uncertainty). However, the uncertainty estimation showed that actually, the first method was the one characterized by lower MU value, indicating that the second method was associated with higher contribution of the type B uncertainty. These results are a good way to show that MU provides additional valuable information for the method performances and interpretation of the obtained analytical results.

Key words: measurement uncertainty, UV-VIS spectrophotometry, enrofloxacin

References:

[1] Marcus Augusto Lyrio Traple, Alessandro Morais Saviano, Fabiane Lacerda Francisco, Felipe Rebello Lourenco; Measurement uncertainty in pharmaceutical analysis and its application; *J. Pharm. Anal.* **Vol. 4(1)** (2014): 1-5.
[2] JCGM 100:2008, *Evaluation of measurement data — Guide to the expression of uncertainty in measurement*, Joint Committee for Guides in Metrology, 2-8, 2008.

SYNTHESIS, CHARACTERIZATION AND THE USE OF SUBSTITUTED ARYLDIAZONIUM SALTS FOR THE MODIFICATION OF THE ACTIVATED CARBON POWDER

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The generation of vey reactive phenyl radicals by the dediazonation (by reducing agents in solution, electrochemistry, UV irradiation, sonication, etc.) of the aryldiazonium it’s a well-established surface modification strategy for grafting for the conducting, semi-conducting and insulating surfaces [1]. The reaction of the formed phenyl radicals leads to the covalent bonding to the surface, enabling a simple route for the surface tailoring with the desired functionalities of the material.

The study involved the synthesis of several aryl the diazonium salts with different functional groups. In the synthetic step, the amines (p –H, $–CH_3$, $–NO_2$, $–SO_3H$, and –COOH aniline) were dissolved in aqueous HBF_4 and then diazotized with sodium nitrite. After the characterization of the synthesized diazonium salts by ATR-IR spectroscopy (using diamond crystal) and cyclic voltammetry (by analyzing their reduction waves onto GC and Pt electrodes in aqueous acidic or organic ACN media + NBu_4BF_4 as supporting electrolyte), they were used for surface modification of active carbon powder (ACP). To achieve the surface modification, to the suspension (0.1M HCl) of continuously stirred ACP the addition of iron powder lead to the formation the formation of highly reactive p-substituated phenyl radicals that were prone to covalent surface binding - giving the modified ACP-Ph-X layer (p –H, $–CH_3$, $–NO_2$, $–SO_3H$, and –COOH). To ascertain the surface modification, the modified ACP-Ph-X was studied using the FT-IR spectroscopy (KBr pellet). The modified surfaces afterwards were successfully used for the adsorption of the Lindane pesticide.

Key words: Lindane, diazonium salts, adsorption, phenyl radicals, GC-ECD.

References:

[1] Avni Berisha , Mohamed M . Chehimi , Jean Pinson , and Fetah I . Podvorica, *Electroanalytical Chemistry A Series of Advances: Volume 26 (Chapter 3. Electrode Surface Modification Using Diazonium Salts)*, Edited by Allen J. Bard and Cynthia G. Zoski, CRC Press 2015.

INFLUENCE OF SILVER SUBSTITUTION ON ELECTROCATALITYC PROPERTIES OF $LaCo_{0.5}Fe_{0.5}O_3$PEROVSKITE

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The perovskite materials are among most versatile known materials. Namely, the number of different perovskites is very large as well as their possible uses. This is mainly a result of flexibility of perovskite structure that can incorporate almost all elements from periodic table, as well as, some organic cations. As outcome, these materials exhibit different properties, as ferroelectricity, piezoelectricity, catalytic activity, superconductivity, photoconductivity etc. The investigations of the catalytic properties of perovskites showed that the best performance have perovskites with transition metal ion (especially, Co, Fe, Mn or Ni) in their structure. Traditionally, one of the most commonly used catalysts is silver. Relying on these finding in our work we combine perovskite materials and silver, and synthesised Ag-substituted perovskites.

In this study we have synthesised $LaCo_{0.5}Fe_{0.5}O_3$ and two Ag-doped perovskites: $La_{0.95}Ag_{0.05}Co_{0.5}Fe_{0.5}O_{3-\delta}$ and $La_{0.9}Ag_{0.1}Co_{0.5}Fe_{0.5}O_{3-\delta}$. The perovskites were synthesised by solution combustion method using citric acid as a fuel. The as-synthesized powders were additionally heated 8 h at 900 °C. The obtained compounds were identified by X-ray powder diffraction (PXRD). The XRD patterns showed that using this synthesis method the compounds of perovskite structure were obtained and that lanthanum can be partially substituted with silver.

The electrocatalytic properties were studied using cyclic voltammetry. The voltammetric response of the obtained perovskites attached on PIGE (paraffin impregnated graphite electrode) and immersed in different solutions (as KOH, KCl, $C_6H_{12}O_6$ etc.) was recorded. The analysis of the recorded voltammograms showed that the obtained perovskites exhibit electrocatalytic activity in solutions containing HO^-, Cl^- ions and glucose.

Key words: complex perovskites, Ag-doped perovskites, X-ray powder diffraction, cyclic voltammetry.

1,3-DIOXANE DERIVATIVES AS INTERMEDIATES FOR CHEMICALLY AND PHOTOCHEMICALLY ACTIVATED MOLECULAR DEVICES

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Molecular machines have been widely investigated during the last decades due to their ability to mimic at molecular level certain macroscopic devices, as a mechanical response to specific external stimuli.

Starting from several examples of chemical pedals, already reported in the literature, the aim of this work was to design, synthetize and investigate the operating mechanism of new molecular devices pursuing possible biomimetic properties. The general components of the two molecular machines subjected to investigation are illustrated in Figure 1.

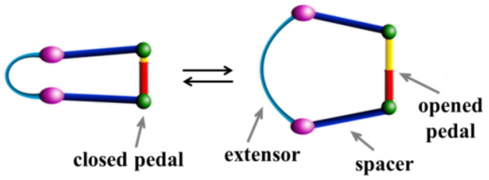

Figure 1. General components of a molecular device

For the two pedals assessed during this study, the application of a chemical (bipyridine unit)[1] or photochemical (azobenzene unit)[2] stimulus leads to a conformational change of the bis-1,3-dioxanic unit (extensor). The movement performed from the axial-axial conformer (decomplexed bipyridine/trans-azobenzene) to the equatorial-equatorial one (complexed bipyridine/cis-azobenzene) can be compared to the contraction-relaxation motion of a muscle cell.

Key words:molecular devices, photoisomerisation, complexation-decomplexation

References:
[1] G. Haberhauer, *Angew. Chem. Int. Ed.* **2008**, *47*, 3635-3638.
[2] E. Merino, M. Ribagorda, *Beilstein J. Org. Chem.***2012**, *8*, 1071–1090.

THE ROLE OF SURFACTANTS (TRITON X-100 AND SODIUM DODECYLBENZENESULFONATE) ON THE ELECTROCHEMICAL DETERMINATION OF ASCORBIC ACID

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Vitamin C has an important role in processes of oxidation and reduction in the human organism by participating in diverse metabolic reactions. The determination of this molecule in different samples has a huge importance and is frequently achieved through the HPLC, UV-VIS, electrochemical methods, etc. The electrochemical determination of vitamin C was done through the use of the cyclic voltammetry on Palm Sens (potentiostat/galvanostat) instrument. The experiments were performed in a conventional single-compartment three-electrode cell. A Platinum electrode was employed as a working, Platinum foil was employed as an auxiliary electrode and Ag/AgCl was used as a reference electrode. The calibration curves were constructed in the vitamin C solution [a). in absence, b. in presence of 5% Triton X-100 or c. 5% sodium dodecylbenzenesulfonate] at the concentration range from 1mM up to 600 mM. The addition of surfactants increases the sensitivity for the determination of these molecules. The electrochemical determination was successfully applied for the determination of the content of this molecule in different samples.

Key words: cyclic voltammetry, Vitamin C, surfactants, limit of detection.

SYNTHESIS AND IDENTIFICATION OF SOME GUANIDINIUM ORGANIC-INORGANIC PEROVSKITES

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Hybrid organic-inorganic perovskites are compounds that may be described with general formula AMX_3, where A is an organic cation, M is metal cation (as Pb^{2+}, Cd^{2+}, Sn^{2+} etc.) and the position of the anion (X) is usually occupied by halide ion. While known for several decades, hybrid organic-inorganic perovskites have only in recent years emerged as extremely promising semiconducting materials especially for solar energy applications. The best photovoltaic properties have been found in perovskites that contain small organic cation. There is a growing interest in searching for new organic-inorganic perovskite.

One small organic cation that could be inserted in perovskite structure is the guanidinium cation, $[C(NH_2)_3]^+$ (Gu).We attempted to synthesize several compounds that contained guanidinium ion: $GuSnCl_3$, $GuPbCl_3$, $GuCd(HCOO)_3$ and $GuSnBr_3$. From the listed compounds only one was known in the literature, $GuSnCl_3$ [1]. The selected combination of cations and anions was based on the value of tolerance factor, *t*. Namely, in order to obtain compound with perovskite structure the value of *t* should be near 1. In studied compounds, $GuSnCl_3$, $GuPbCl_3$, $GuCd(HCOO)_3$ and $GuSnBr_3$, their values are 1.096, 1.082, 0.919 and 1.078, correspondingly. The synthesis methodology, the solvents and temperature of synthesis were varied depending on the properties of starting materials. All compounds were identified by combination of X-ray powder diffraction and IR spectroscopy. The XRD patterns were used to obtain information about the purity of obtained products, while the IR spectra were mainly used to detect the presence of the organic cation. The combined results showed that in all cases we have obtained new compounds and the IR spectra showed the characteristic bands of the guanidinium cation.

Key words:organic-inorganic perovskites, guanidinium ion, XRPD, IR spectroscopy.

References:
[1] M. Szafrański, K. Ståhl, *J. Solid State Chem.*, **180** (2007) 2209–2215.

THE ELECTROCHEMICAL MONITORING OF ‘‘EX SITU‘‘ EXTRACTED VITAMIN C

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Vitamin C (Ascorbic acid – AA) is a water soluble vitamin that has a major role for the human health (bone formation, wound healing, antioxidant, enzyme cofactor, etc.). The precise determination of these compounds in different samples is very important. Generally there is vast number of instrumental techniques for determination of vitamin C (HPLC, UV-VIS, ect.), one of methods used frequently for this purpose is cyclic voltammetry. The content of vitamin C was evaluated by cyclic voltammetry using a standard there electrode cell (Pt, Ag/AgCl, Pt – foil). In the first step by evaluating the oxidation current of standard solutions with concentration from 1 – 600 mM a calibration curve was constructed ($y = 18.229x + 508.65$, $R^2 = 0.987$).

The content of vitamin in real samples was determined after the extraction from aqueous solution by calibration curve and by standard addition method. The addition of different surfactants in the solution was also studied. The surfactants increased the detection limit of the AA.

Key words: Vitamin C, cyclic voltammetry, surfactants, limit of detection.

THE USE OF THE GRAFTED ACTIVATED CARBON POWDERS FOR THE ADSORPTION OF THE LINDANE PESTICIDE FROM MODEL SYSTEMS

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The pollution of environment (air, water and soil) by organic and inorganic species represents a severe problem that needs to be addressed seriously. The technologies based in the adsorption presently are being used largely for the removal of such pollutants from wastewaters. Although there is a huge number of different adsorbent systems that can be used for the removal of pollutants from wastewaters, activated carbon powder (ACP) is most commonly used in industrialized countries. The adsorption of organochlorine pesticides onto ACPs, have attested to be the most efficient way for the removal of the dissolved pesticides.

In our present study we used modified ACP for the adsorption of Lindane from hexane solutions. In the modification step, the ACP powder was stirred in a beaker containing mM amount of the corresponding synthesized diazonium salt dissolved in acidic aqueous media (p-methyl-, phenyl-, p-sulfonic and p-nitrobenzendiazoniumtetrafluoroborate) and afterward was reduced by the addition of the micrometric sized iron powder. The addition of iron powder leads to the formation the formation of highly reactive p-substituated phenyl radicals that are prone to covalent surface binding - giving the modified ACP-Ph-X layer (X= -H, -CH_3, -SO_3H and -NO_2) [1]. The modified ACP powders were successfully use for the adsorption of the Lindane (gamma-hexachlorocyclohexane, γ-HCH). In the adsorption study, the concentration of Lindane was assessed by the use of GC-ECD technique. The gathered adsorption data for this molecule show that this process is dependent on the surface attached groups of the ACP powder.

Key words: Lindane, diazonium salts, adsorption, phenyl radicals, GC-ECD.

References:

[1] Avni Berisha , Mohamed M . Chehimi , Jean Pinson , and Fetah I . Podvorica, *Electroanalytical Chemistry A Series of Advances: Volume 26 (Chapter 3. Electrode Surface Modification Using Diazonium Salts),* Edited by Allen J. Bard and Cynthia G. Zoski, CRC Press 2015.