MatCatNet Workshop
“From Molecules to Functionalised Materials“

Scientific module “Polymers”
5-10 September 2014, Ohrid, Macedonia

Sponsored by:
INTERNATIONAL MASTER AND POSTGRADUATE PROGRAMME IN MATERIALS SCIENCE AND CATALYSIS

MatCatNet

05.09-10.09.2014

Ohrid, Macedonia

“Ss. Cyril and Methodius” University

Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Skopje, Macedonia
PROGAMME

MatCatNet Workshop
“From Molecules to Functionalised Materials”
Scientific module “Polymers”
5-10 September, 2014, Ohrid, Macedonia

Friday, 5 September 2014
09.00   Registration

10.30   Prof. Valentin Mirčeski
        Welcoming address

10.35   Prof. Luminita Silaghi-Dumitrescu
        Overview of the project

Scientific module “Polymers”
-Lectures-

11:00-12:00  Ass. Prof. Avni Berisha (Prishtina)
            Polymers – a basic introduction

12:00-13:00  Prof. Luminita Silaghi-Dumitrescu (Cluj-Napoca)
            Organometallics in polymer chemistry

13:00-14:30  Lunch

14:30-16:30  Prof. Valentin Mirčeski (Skopje)
            Electrochemical techniques for studying conducting polymers

16:30-16:45  Coffee Break
16:45-17:45  Prof. Rubin Gulaboski (Štip)
Voltammetry of conducting polymers

Saturday, 6 September 2014

09:00-10:00  Prof. Fetah Podvorica (Prishtina)
Electrografting of polymers onto material surfaces

10:00-11:00  Prof. Blaga Radovanović (Niš), Ass. Prof. Marjan Randjelović (Niš)
Investigation of rubber-filler interactions of nano- and micro-filled crosslinked polymer blends

11:00-11:15  Coffee Break

11:15-12:15  Assoc. Prof. Dragan Djordjević (Niš)
Geopolymers

12:15-13:15  Ass. Prof. Luljeta Raka (Tetovo)
Synthesis, structure and properties of polypropylene/clay nanohybrids

13:15-14:45  Lunch

14:45-15:45  Prof. Gordana Bogoeva-Gaceva (Skopje, invited lecturer)
Interface in polymer composite materials

15:45-16:45  Ass. Prof. Vineta Srebrenkoska (Štip)
Preparation and recycling of polymer eco-composites

16:45-17:00  Coffee Break

17:00-18:30  Assoc. Prof. Vladimir Ivanovski (Skopje)
IR spectroscopy of polymers
18:30-20:00  Sightseeing of Ohrid old city  
(walking tour I)

Sunday, 7 September 2014

09:00-11:00  Prof. Muriel Hissler (Rennes, invited lecturer)  
π-conjugated polymers for (opto)electronic devices

MatCatNet Workshop

-Students’ oral presentations-

(chair: Jeton Halili)

11:00  Miha Bukleski  
(Faculty of Natural Science and Mathematics, “Ss. Cyril and Methodius” University,  
Skopje, Macedonia)  
Quantification of the maximal chemisorbed 3-aminopropylsilyl groups on silica gel using DRIFT spectroscopy

11:15  Mihaela Vasile  
(Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca, Romania)  
The evaluation of absorption of carbon dioxide in alkanolamines through dynamic modeling

11:30  Egzon Ademi  
(Faculty of Natural and Mathematical Science, State University of Tetovo, Tetovo, Macedonia)  
Coupling of some six membered heterocycles with 4-hydroxycoumarin through the hydrazinylidene link

11:45-12:00  Coffee Break
(chair: Vladimir Radovanović)

12:15  Jeton Halili  
(Faculty of Natural Science, University of Prishtina, Prishtina, Kosovo)  
Supercritical CO₂ extraction of heavy metals from aqueous solution by using chelate ligand - dithizone

12:30  Adrian Brânzannic  
(Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca, Romania)  
Archaeometric studies on ancient oxidic materials from Romania

12:45  Katerina Stankoska  
(Faculty of Natural Science and Mathematics, “Ss. Cyril and Methodius” University, Skopje, Macedonia)  
Studying CE mechanism at three-phase electrode, where coupled electron-ion transfer is complicated by complexation of the transferring ion

13:00-14:00 Lunch

(Chair: Sasho Stojkovikj)

14:00  Zulihaje Ismaili  
(Faculty of Natural and Mathematical Science, State University of Tetovo, Tetovo, Macedonia)  
High density-polyethylene for pharmaceutical industry: thermal characterization

14:15  Nikolina Mitreska  
(Faculty of Natural Science and Mathematics, “Ss. Cyril and Methodius” University, Skopje, Macedonia)  
Hydroxylated derivatives of coenzyme Q₄ as ligands for complexation of transition metals

14:30  Jeta Sela  
(Faculty of Natural and Mathematical Science, State University of Tetovo, Tetovo, Macedonia)  
Synthesis and characterization of Co(II) and Ni(II) complexes with schiff bases derived from salicylaldehyde
14:45  Dijana Jadreško  
(Faculty of Natural Science and Mathematics, “Ss. Cyril and Methodius” University, Skopje, Macedonia)  
Characterization of electrode processes by cyclic square-wave voltammetry (CSWV)

15:00  Valdrin Januzaj  
(Faculty of Natural Science, University of Prishtina, Prishtina, Kosovo)  
Composite electrodes with carbon supported Ru-nanoparticles for H₂O₂ detection

15:15  Violeta Ivanova-Petropoulos  
(Faculty of Agriculture, University “Goce Delčev”, Štip, Macedonia)  
Multi-element analysis of wines

15:30-16:00  Coffee Break

16:00-17.00  Project coordinators meeting  
Evaluation of the project and future perspectives of the network

17:00-19:00  Sightseeing of Ohrid old city  
(walking tour II)

Monday, 8 September 2014

09:00-10:00  Prof. Muriel Hissler (Rennes, invited lecturer)  
Phosphole-based compounds for optoelectronic applications

-Students’ oral presentations-

(Chair: Mihaela Vasile)

10:00  Njomza Buxhaku  
(Faculty of Natural and Mathematical Science, State University of Tetovo, Tetovo, Macedonia)  
Hydrothermal reaction of tripoli with calcium hydroxide
10:15  Biljana Balabanova  
(Faculty of Medical Science, “Goce Delčev” University, Štip, Macedonia)  
Characterization of macro and trace elements contents in edible oils with application of microwave digestion and ICP-MS

10:30  Sasho Stojkovikj  
(Faculty of Natural Science and Mathematics, “Ss. Cyril and Methodius” University, Skopje, Macedonia)  
Development of nonenzymatic amperometric sensor for detection of hydrogen peroxide based on Manganese(II) carbonate thin films

10:45  Abibe Useini  
(Faculty of Natural and Mathematical Science, State University of Tetovo, Tetovo, Macedonia)  
Baylis-hillman reactions catalyzed by hexamethylenetetramine

11:00  Szőke Árpád Ferenc  
(Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca, Romania)  
The incubation of indigo carmine in sol-gel coatings

11:15-11:30 Coffee Break

-Students’ Poster Flash Presentations-

(Chair: Arianit Reka)

11:30  Elena Drakalska  
(Faculty of Medical Science, “Goce Delčev” University, Štip, Macedonia)  
Preparation and characterization of polyoxythylated tert-buthylcalix[4]arene nanoparticles as platforms for delivery of curcumin

11:40  Ivana Vuchkovikj  
(Faculty of Natural Science and Mathematics, “Ss. Cyril and Methodius” University, Skopje, Macedonia)  
Study of nitrogen pollution in Croatia by moss biomonitoring and Kjeldahl method
11:50  Nikola Stojkovic  
(Faculty of Science and Mathematics, University of Niš, Niš, Serbia)  
Preparation and photocatalytic activity of templated mesoporous TiO\textsubscript{2} thin films with selected polymers

12:00  Belinda Aliu  
(Faculty of Natural and Mathematical Science, State University of Tetovo, Tetovo, Macedonia)  
Synthesis of ferum complexes with 3-[2-(thiazol-2-yl)hydrazinylidene]chroman-2,4-dione

(Chair: Biljana Balabanova)

12:10  Viktorija Maksimova  
(Faculty of Medical Science, “Goce Delčev” University, Štip, Macedonia)  
Electrochemical behavior of capsaicin and its anti-oxidative properties studied by means of cyclic voltammetry

12:20  Milica Stankovic  
(Faculty of Science and Mathematics, University of Niš, Niš, Serbia)  
Cornelian cherry fruit and leaf extracts as potential drugs

12:30  Luana Radu  
(Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University, Cluj-Napoca, Romania)  
Noncovalent interactions between hemoglobin and compounds with potential biological activity

12:40  Marija Sterjova  
(Faculty of Medical Science, “Goce Delčev” University, Štip, Macedonia)  
Evaluation radiochemical purity of $^{177}$Lu-labelled rituximab conjugates using HPLC method

12:50  Dora Chisalita  
(Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University, Cluj-Napoca, Romania)  
Lower rim functionalized calix[8]arenes coupling to silica surface
13:00  Vladimir Radovanovic  
(Faculty of Science and Mathematics, University of Niš, Niš, Serbia)  
Optimization of ultrasonic extraction of polyphenols from grape waste using design expert software

13:10  Arianit Reka  
(Faculty of Natural and Mathematical Science, State University of Tetovo, Tetovo, Macedonia)  
Low temperature reaction of amorphous SiO₂ with calcium hydroxide

13:30-14:30 Lunch

14:30-18:00 Guided tour to the Monastery St. Naum and springs of Ohrid’s Lake

20:00  Gala Dinner

Tuesday, 9 September 2014  
(Chair: Adrian Branzanic)

09:00  Liridona Useini  
(Faculty of Natural and Mathematical Science, State University of Tetovo, Tetovo, Macedonia)  
Synthesis of 4-aryl/alkylaminocoumarines by using microwave

09:10  Stefan Mihajlovic  
(Faculty of Science and Mathematics, University of Niš, Niš, Serbia)  
Effect of selective removal of grapevine leaves of cabernet sauvignon polyphenolic content

09:20  Tanja Dimitrova  
(Faculty of Natural Science and Mathematics, “Ss. Cyril and Methodius” University, Skopje, Macedonia)  
Microwave-assisted organic synthesis of some N-alkyl substituted isatin 3-thiocarbohydrazones
09:30 Marija Atanasova
(Faculty of Medical Science, “Goce Delčev” University, Štip, Macedonia)
Determination of oxidative status in EDTA plasma of hemodialysis patients by peroxide assay

09:40 Milica Ristic
(Faculty of Science and Mathematics, University of Niš, Niš, Serbia)
Geochemical analysis of trace metals: Sokobanja limestone

09:50 Rudina Veliu
(Faculty of Natural and Mathematical Science, State University of Tetovo, Tetovo, Macedonia)
Baylis-hillman reactions catalyzed by hezamethylenetetramine

10:00 Vicentiu Taciuc
(Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca, Romania)
Mechanistic investigations of undesired prooxidant reactions in compounds and natural extracts with antioxidant activity

10:10 General discussion on poster results

12:00-14:00 Lunch

14:00 Award Ceremony, Closing remarks

15:00 Social event

Wednesday, 10 September 2014

09:00 Departure
SCIENTIFIC AND METHODS MODULE

“POLYMERS”
SCIENTIFIC AND METHODS MODULE

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<th>Polymers</th>
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<tr>
<td>Number</td>
<td>2014-MatCatNet03</td>
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<tr>
<td>Aims</td>
<td>The module aims at providing the participants with some detailed understanding of polymers. Lectures cover historical aspects, basic definitions, structure and classification, polymer formation mechanisms based on step-growth, chain-growth polymerization, Ziegler-Natta polymerization, Ring Opening Polymerization (ROP), Ring Opening Metathesis Polymerization (ROMP), etc. The following aspects will be also highlighted: - commercially important polymers - conducting polymers, ionomers, dendrimers, etc. as well as novel applications of these materials - most frequently used electrochemical techniques for studying conducting and redox-active polymers - most important examples of conductive polymers used in electrochemistry focusing on their features and applications - polymer electrografting methods, electrografting of polymer conductors - cross-linking polymer systems - geopolymers - polymer composite materials - polymer/clay nanohybrids</td>
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<tr>
<td>Basics</td>
<td>Basic knowledge of organic, inorganic chemistry; basic understanding of electrochemical experiments; electrochemistry; organometallic compounds, transition metal complexes; nanoparticles; basic knowledge of analytical and physical chemistry</td>
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<tr>
<td>Contents</td>
<td>Aspects of polymer chemistry</td>
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<td>Type</td>
<td>Two-day block course</td>
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<td>Time</td>
<td>Day 1: 11:00 – 17:45, Day 2: 9:00 – 18:00, Day 3: 9:00 – 10:00</td>
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<td>Work load</td>
<td>15 contact hours/ 45 hours self-study</td>
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<td>Examination</td>
<td>written</td>
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<td>Credit points</td>
<td>2</td>
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Responsible scientists
Valentin Mirceski (MK), Rubin Gulaboski (MK), Luminita Silaghi-Dumitrescu (RUM), Avni Berisha (KOS), Fetah Podvorica (KOS), Blaga Radovanovic (SER), Dragan Djordjevic (SER), Marjan Randjelkovic (SER), Luljeta Raka (MK),

Guest lecturers
Gordana Bogoeva-Gaceva (MK), Muriel Hissler (FR);

Recommendations for literature, e-learning
- C. E. Carraher Jr., Carraher's Polymer Chemistry, CRC Press, 2013
- R. J. Young, P. A. Lovell Introduction to Polymers, CRC Press, 2011
- S. Gabriel, R. Jérôme, C. Jérôme, Progress in Polymer Science 2010, 35, 113-140
- V. Kinzig, B. J. Kinzig, Composite application. The role of matrix, fiber and interface, VCH Publ. Inc., 1992
- D. R. Paul, L. M. Robeson, Polymer 2008, 49, 3187-3204
- L. Raka, G. Bogoeva-Gaceva, K. Lu, J. Loos, Polymer 2009, 50, 3739-3746
- G. W. Coates, Chem. Rev. 2000, 100, 1223-1252
- M. R. Buchmeiser, Chem. Rev. 2000, 100, 1565-1604
- O. Nuyken, S. D. Pask, Polymers 2013, 5, 361-403
<table>
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<tr>
<th>Time</th>
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<td>Avni Berisha (Prishtina)</td>
<td>Polymers – a basic introduction</td>
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<td>Luminita Silaghi-Dumitrescu (Cluj-Napoca)</td>
<td>Organometallics in polymer chemistry</td>
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<td>Valentin Mirceski (Skopje)</td>
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<td>16:45-17:45</td>
<td>Rubin Gulaboski (Stip)</td>
<td>Voltammetry of conducting polymers</td>
<td>Ohrid, MK</td>
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<td><strong>Day 2</strong></td>
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<td>09:00-10:00</td>
<td>Fetah Podvorica (Prishtina)</td>
<td>Electrografting of polymers onto material surfaces</td>
<td>Ohrid, MK</td>
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<td>10:00-11:00</td>
<td>Blaga Radovanovic (Nis), Marjan Randjelcovic (Nis)</td>
<td>Investigation of rubber-filler interactions of nano- and micro-filled crosslinking polymer blends</td>
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<td>11:15-12:15</td>
<td>Dragan Djordjevic (Nis)</td>
<td>Geopolymers</td>
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<td>12:15-13:15</td>
<td>Luljeta Raka (Tetovo)</td>
<td>Synthesis, structure and properties of polypropylene/clay nanohybrids</td>
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<td>Gordana Bogoeva-Gaceva (Skopje, invited lecturer)</td>
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<td>15:45-16:45</td>
<td>Vineta Srebrenkoska (Stip)</td>
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<td>17:00-18:00</td>
<td>Vladimir Ivanovski (Skopje)</td>
<td>IR spectroscopy of polymers</td>
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<td>09:00-10:00</td>
<td>Muriel Hissler (Rennes, invited lecturer)</td>
<td>Synthesis of organic polymers for opto-electronic applications</td>
<td>Ohrid, MK</td>
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Polymers - a basic introduction

Avni Berisha

University of Prishtina ”Hasan Prishtina”, Faculty of Natural Sciences and Mathematics, Department of Chemistry, Prishtina, Republic of Kosovo, avni.berisha@uni-pr.edu

Polymers, are a large class of materials consisting of numerous small molecules (called monomers), that can be linked together to form long chains, and thus are also known as macromolecules. By recognizing that these compounds make up many important natural materials, scientists created synthetic analogues possessing a variety of interesting properties. Many eras have been characterized by the materials that were then important to human society (e.g. stone age, bronze age and iron age). The 20th century has gained numerous labels of this type, counting the nuclear age and the oil age; however, the best name is likely the plastic or polymer age. In this period no technological advancement has impacted our lives more than the widespread use of synthetic plastics in our construction materials, automobiles, clothes, dishes, packaging, and toys, to name but a few. Truly, the applications of these materials as flexible films, fibres, resistant paints, adhesives and tough but light solids has transformed modern society.

In the framework of this lecture some historical aspects linked to polymer science, followed by basic definitions, structures and classifications regarding polymeric materials shall be presented. Then the formation mechanisms of polymers based on step-growth and chain-growth polymerization will be discussed together with a short introduction mentioning the use of some commercially important polymers such as polyethylene, polystyrene, polyvinylchloride, nylon, poly(ethylene terephthalate), etc. The last section will also highlight some aspects of interesting polymers (conducting polymers, ionomers, dendrimers, etc) as well as novel applications of these materials (in drug delivery, photovoltaics, as support materials, thin films, etc).

References:
Organometallics in polymer chemistry

Luminita Silaghi-Dumitrescu

Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, Cluj-Napoca, Romania, lusi@chem.ubbcluj.ro

This lecture gives an overview of the main aspects of the use of organometallic compounds of transition metals in polymer chemistry. The following topics will be presented:

• Ziegler-Natta polymerization: - Catalysts; - The mechanism of Ziegler-Natta polymerization; - Recent developments in Ziegler-Natta polymerization

• Ring-Opening Polymerization (ROP) is the chain-growth polymerization, in which the terminal end of a polymer chain acts as a reactive centre where further cyclic monomers can react by opening its ring system and form a longer polymer chain. ROP is the most versatile method of synthesis of major groups of biopolymers, particularly when they are required in quantity. The driving force for the ring opening of cyclic monomers is via the relief of ring strain or steric repulsions. Cyclic monomers that are polymerized using ROP include: alkanes, alkenes, compounds containing heteroatoms in the ring (oxygen: ethers, acetals, esters, and anhydrides; sulfur: polysulfur, sulfides and polysulfides; nitrogen: amines, amides (lactames), imides, N-carboxyanhydrides and 1,3-oxaza derivatives; phosphorus: phosphates, phosphonates, phosphites, phosphines and phosphazenes, silicon: siloxanes, silaethers, carbosilanes and silanes). The mechanisms of ROP: radical ring-opening polymerization, anionic ring-opening polymerization, cationic ring-opening polymerization, will be discussed.

• Ring-Opening Metathesis Polymerization (ROMP): - Catalysts for ROMP; - Homogeneous Metathesis Polymerization by well-defined group 4 and group 8 transition-metal alkylidenes; - Copolymerization

The aims of this lecture are to understand the role of the organometallic compounds in polymerization processes.

References:
Electrochemical techniques for studying conducting polymers

Valentin Mirceski

“Ss Cyril and Methodius” University, Faculty of Natural Sciences and Mathematics, Skopje, Republic of Macedonia, valentin@pmf.ukim.mk

The main goal of the lecture is to provide a basic knowledge of the most frequently used electrochemical techniques for studying conducting and redox-active polymers, such as chronoamperometry, chronocoulometry and transient techniques such as cyclic voltammetry and square-wave voltammetry. The lecture will cover the basic principles of electrochemical experiments, addressing the phenomena of electrode polarization and electrode kinetics, as well as the basic principles besides the above-mentioned techniques, applied for studying conventional electrode processes of a dissolved redox couple, as well as processes specifically relevant to redox-active and conducting polymers. For the latter, the electrode mechanism of thin films immobilized on the electrode surface will be analyzed. For cyclic and square-wave voltammetry, particular attention will be given to methods for uncovering the electrode mechanisms, providing diagnostic criteria for recognizing reversible, totally irreversible and and quasireversible electrode reactions, electrode reactions coupled with chemical reactions, as well as electrode mechanism of a surface confined redox couple with and without lateral interactions, relevant to the polymer electrochemistry.

References:
Voltammetry of conducting polymers

Rubin Gulaboski

Faculty of Medical Sciences, Goce Delcev University Stip, Macedonia, rubin.gulaboski@ugd.edu.mk

The search for new materials for enhancing electrical conductivity of various materials is one of the most active research areas today. Conducting polymers represent a unique class of organic materials that have been used in many applications such as bioelectronics, sensors, corrosion protection, electrocatalysis, and energy storage devices. Application of the conductive polymers in electrochemistry is almost inevitable in order to get better features of the voltammetric systems studied. Besides facilitating electron transfer reactions, conductive polymers are a suitable platform for anchoring both lipophilic and hydrophilic analytes, while facilitating (often significantly) their redox transformation. An insight into the most important examples of conductive polymers used in electrochemistry will be given, while also focusing on their features and applications, and the processes of electropolymerization. Novel conductive polymers and their potential application will also be discussed.

References:
Electrografting of polymers onto material surfaces

Fetah I. Podvorica

University of Prishtina ‘‘Hasan Prishtina’’, Faculty of Natural Sciences and Mathematics, Department of Chemistry, Prishtina, Republic of Kosovo, fetah.podvorica@uni-pr.edu

Polymer films can be grafted on conductor and semiconductor surfaces via electrochemistry. The term electrografting means the initiation of the polymer grafting reaction through the oxidation or reduction of the monomer.[1a] This method permits to strongly attach polymer films to a variety of substrates including carbon, metals and their oxides, but also dielectrics such as polymers. Attached organic layers may impart a high number of surface properties like that of wettability, adhesion, corrosion protection, microelectronics, biomedical engineering, etc.[1b] In order to increase the strength of the interface interaction, in many cases, coupling agents like silanes and thiol self-assembled monolayers were used because they provide a chemical adsorption of the organic layer on the substrate surface.[1c]

Polymer electrografting methods, either by reduction or oxidation, have been developed since 1980 and now some of them have reached an industrial stage such as biomedical implants and different electronic devices.[1,2] The cathodic electrografting of acrylonitrile in metals and the anodic electrografting of polymer conductors like pyrrole and thiophen will be explained. Attached organic layers that provide a vinylic monomer or a diazonium salt may be used as the initiators for further polymerization in the case of Atom Transfer Radical Polymerization (ATRP).[2] One of the main advantages of electrografting over coupling agents is the high control the density of the grafting layer. Although the experimental conditions to modify the material surface with polymers require only basic electrochemical equipment, electrografting has not yet received much attention and we would like to elucidate and stress its potential.

References:
Rubber-filler interactions of nano- and micro-filled crosslinked polymer blends

Blaga Radovanović, Marjan Randjelović

University of Niš, Faculty of Natural Sciences and Mathematics, Višegradska 33, 18000 Niš, Serbia, e-mail: blaga_radovanovic@yahoo.co.uk

The lecture will focus on rubber-filler interactions of nano- and micro-filled cross-linked polymer blends based on chlorosulfonated polyethylene rubber (CSM) and polychloroprene rubber (CR) reinforced by nano- and micro- filler.

Active precipitated silica ($\text{SiO}_2$) with particle size 15 nm and diatomaceous earth with 28 $\mu$m were used as fillers. Conventional vulcanisation was performed and the physico-mechanical properties of the CR/CSM/$\text{SiO}_2$ cross-linked polymer systems were determined.

The morphology of the fracture surface of investigated materials crosslinked in the presence of sulfur, ethylenethiourea and magnesium oxide was studied by Scanning Electron Microscopy (SEM).

Filler-rubber interactions of nano- and microfilled CR/CSM crosslinked polymer blends was studied by FT infrared (IR) spectroscopy by ATR (Attenuated Total Reflectance). Infrared measurements revealed the formation of chemical bonds between the surface of the $\text{SiO}_2$ and the CR/CSM matrix after heat treatment at 160 °C. The nano-filled crosslinked polymer matrix has a strong peak at 1079 cm$^{-1}$ in the IR spectra resulting from the SiO-C vibration.

Blending of two or more types of polymer is a useful technique for the preparation and development of materials with properties superior to those of individual constituents.

References:


Geopolymers

Dragan M. Đorđević

Laboratory for Geochemistry, Cosmochemistry and Astrochemistry, Faculty of Natural Sciences and Mathematics, University of Niš, Višegradska 33, 18000 Niš, Serbia, e-mail: dragance73@yahoo.com

Genesis of sedimentary organic matter (OM) creates so-called geopolymers. Depending on the nature of the starting material from which they arise and their development path, geopolymers are composed of kerogen and bitumen, which includes asphaltenes, resins and polar fractions.

Division of geopolymers in kerogen, asphaltenes, resins and polar fraction was carried out on the basis of their solubility in organic solvents. Kerogen is a part of the sedimentary OM which is insoluble in organic solvents and it is not hydrolysed in mineral acids and alkalis. Asphaltenes, resins, and the polar fractions, in contrast to kerogen, are soluble in organic solvents and are each distinguished by its solubility therein.

The term kerogen is not uniquely determined. It was first used by A. Crum-Brown to describe the organic content of oil shale from a Lothians (Scotland), that gives after distillation oils with a waxy consistency (from the Greek kairos-wax).

In general, insoluble OM represents kerogen.

The essence of the overall changes, biochemical and geochemical processes that expose sedimentation sludge is a steady increase in carbon content in the kerogen. This process is indivisible, but it is possible to distinguish three successive stages.

Asphaltenes are complex polymers composed of polycyclic aromatic or aliphatic rings associated with naphthenic aromatic chains and heteroatoms (N, S, and O). Asphaltenes are much smaller molecules than kerogen but with similar structure and that’s why they can be regarded as small fragments of kerogens structure. They are present in bitumen, asphalt, and crude oil.

Tests have shown that asphaltenes are characterized as micro- and macrostructures. Microstructures are based on polycondensated aromatic systems substituted with alkyl groups, generally -CH₃ groups and have a high content of heteroatoms. The individual layers are typically aromatic arranged one upon the other, in four to six layers, and are connected by π-π bonds. The group of molecules formed in this way is called crystallite and has a molecular mass (MM) of about 1000-10000 Da with the average thickness of 150-200 nm. The MM of a single layer is about 500-1000 Da and its average thickness of 80-100 nm. The macrostructures of asphaltenes or micelles are formed by joining several crystallites. The size of the micelles and their MM are different, depending
on the applied analytical techniques for their isolation. The MM of micelles ranges from 50000 Da or more, depending on the number of crystallites, while their average thickness is 500 nm.

Besides the asphaltenes, the soluble organic fraction contains also resins, geopolymers similar in structure to the asphaltenes. Resins include small amounts of free acids, esters and ethers. They include compounds similar to the asphaltenes but less aromatic. Resins have lower MM than asphaltenes, from 500 to 1200 Da. They are unstable compounds when exposed to air and sunlight. When heated they give hydrocarbons and asphaltenes.[3]

Asphaltenes and resins are present in less than 10% in paraffin (light oil), 10 - 40% in the aromatic (medium heavy) of oil and up to 60% in heavy degraded oil.[3]

References:
Synthesis, structure and properties of polypropylene/clay nanohybrids

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Polymer/clay nanohybrids (PCH) have great potential as low-cost, lightweight and high-performance materials because of the property enhancements due to their improved mechanical, thermal, electrical and optical properties as compared to their macro- and micro-counterparts. Isotactic polypropylene (iPP) is among the most extensively studied thermoplastics with widespread applications, because of its excellent properties and low price. In general, from an industrial point of view, preparation of PCH by melt mixing, using extrusion process, remains the most applicable and acceptable technique. Since iPP is a nonpolar polymer, its direct intercalation into the clay galleries is very difficult or impossible to achieve; the usual result instead is rather poor intercalation, where the layered silicate remains in stacks with expanded galleries.[1] The use of coupling agents mainly based on maleic anhydride grafted PP (PP-g-MA), as well as proper clay modification, have been shown to significantly improve clay intercalation and its dispersion in a polymer matrix.[2]

The effects of clay and polymer modification on the nanohybrid structure, obtained by two different methods - melt intercalation[3] and latex technique[4], in terms of clay dispersion in polymer matrix, its morphology, crystallization behaviour and overall properties will be the subject of this lecture.

References:
Interfaces in polymer composite materials

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In fiber reinforced polymer composites, both fiber and matrix retain their physical and chemical properties. Yet, the mechanical properties of the composite are far above those predicted by the rule of mixture, due to the presence of an interface between these two components. A classical definition of the interface in polymer composites is that “an interface is a surface (two-dimensional entity) formed by the common boundary of reinforcing fiber and polymer in contact which constitutes the bond in-between for transfer of loads”.[1] Recently the fiber/matrix interface is treated as a three-dimensional entity, extending further than the atomic dimensions of the boundary, the properties of which are different from those of the bulk polymer matrix.

Interfacial interactions govern the mechanism of damage accumulation and propagation in composite materials. Among them, the adhesion between the fibers and polymer matrix plays a predominant role, since the stress transfer at the interface requires an efficient coupling between fibers and matrix.[1,2] Besides the numerous techniques and approaches developed for interface characterization, it still represents a least understood component of a composite material. Moreover, the optimization of interfacial bonding is not a simple task, owing to the complexity of the chemical and physical nature of the interface and the variety of roles it is called on to perform.[2]

The nature and properties of the interface are unique to each fiber/matrix system, however, certain common features apply for thermosetting and thermoplastic polymers reinforced with glass, carbon and other fibers, and they will be discussed in this lecture.[2,3]

References:
Preparation and recycling of polymer eco-composites

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The interest in natural fiber-reinforced polymer composites is growing rapidly due to their high performance in terms of mechanical properties, significant processing advantages, excellent chemical resistance, low cost and low density. In this lecture, the compression and injection molding of polypropylene (PP) and polylactic acid (PLA) based composites reinforced with rice hulls or kenaf fibres will be presented and their basic properties will be discussed. Rice hulls from rice processing plants and natural lignocellulosic kenaf fibres from the bast of the plant Hibiscus Cannabinus represent renewable sources that could be utilized for composites. Maleic anhydride grafted PP (MAPP) and maleic anhydride grafted PLA (MAPLA) were used as coupling agents (CA) to improve the compatibility and adhesion between the fibres and the matrix. Investigations of the possibilities for reuse of the polymer eco-composites have been carried out. The eco-composites based on recycled matrices and recycled composites were produced and structure/properties relationships were investigated as a function of the number of reprocessing cycles. As a result of comparison of the composites properties, the polymer eco-composites belong in the category of materials which could be used as non-load bearing construction materials for different industries.

References:
IR spectroscopy of polymers

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Polymers play an enormously important role in modern society. These materials represent the basis to most aspects of today’s modern life like building, communication, transportation, packaging and clothing. Understanding of the structures and different properties of polymers is thus vital. Infrared spectroscopy can be employed in the identification of the composition of polymers, monitoring of the polymerization processes, characterizing polymer structure, examining the polymer surfaces and the investigation of polymer degradation processes. For that purpose, different IR transmission and reflection techniques may be used. The IR spectra obtained using different techniques however, differ due to the difference in the signal detected.

In this lecture, different transmission (pellet, mull, film) and reflection (specular reflectance, ATR, DRIFT) techniques will be presented and their physics explained in short. Furthermore, examples on the usage of these techniques will be given, specified on the investigation of different aspects of polymers (polymerization, structure, surfaces, degradation).

References:
\pi\text{-conjugated polymers for (opto)electronic devices}

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Over the last twenty years \pi\text{-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 p-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.

This lecture will begin with an introduction on 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, a brief introduction on organic light-emitting diodes and solar cells is provided. A special focus will be on the synthesis and properties of molecular and polymeric conjugated materials.

References:
WORKSHOP

“From Molecules to Functionalized Materials”

Oral Presentations
QUANTIFICATION OF THE MAXIMAL CHEMISORBED 3-AMINOPROPYLSILYL GROUPS ON SILICA GEL USING DRIFT SPECTROSCOPY

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The main purpose of using 3-Aminopropyltrimethoxysilane (APTMS) was to functionalize silica gel’s surface for its further use in obtaining ferrocenyl derivative that can exhibit catalytic activity. APTMS has two different functional groups (amino and methoxy moieties) and can thus be used as a coupling agent (spacer), especially on silica gel as shown in Fig. 1.

The modified silica gel products with organic layers are of high importance in the preparation of composite materials with vast applications in synthetic (e.g. catalysts) or analytical chemistry (e.g. electrochemical sensors).

In the present work it was proposed a method for quantitative determination of the attached APTMS molecules as aminopropylsilil (APS) fragments on the silica gel’s surface. The quantification was done by means of the Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy technique. The process was monitored via the appearance and vanishing of the IR bands characteristic for the OH, CH₂ and NH₂ vibrations. The maximum amount of the APS was determined by integrating the spectra in the frequency range of the n(CH₂)/n(CH₃) vibrations between 3014 and 2808 cm⁻¹. The results were further confirmed by elemental analysis for carbon.

![Chemical reaction between the free OH groups from the activated silica gel and APTMS in anhydrous conditions](image)

Figure 1. Chemical reaction between the free OH groups from the activated silica gel and APTMS in anhydrous conditions

Keywords: 3-aminopropyltrimethoxysilane (APTMS), Silica gel, chemisorption, DRIFT spectra, IR studies
THE EVALUATION OF ABSORPTION OF CARBON DIOXIDE IN ALKANOLAMINES THROUGH DYNAMIC MODELING

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Carbon capture and storage is one of the most effective way to reduce CO₂ emissions from fossil fuel consumption and to stabilize the atmospheric concentration of CO₂. Among various CCS technologies, the absorption of carbon dioxide in monoethanolamine is considered as potential solution to reduce the CO₂ from the atmosphere. The basic idea of this process is to use a MEA solution as a absorber of CO₂ in a absorption column.

The carbon dioxide is captured by its reaction with monoethanolamine in an absorption column at a pressure of 1 bar and a temperature of 30 degrees Celsius and removed at different physical conditions through desorption. The solution of MEA obtained in the desorption column is then returned in the absorber to be reused.

The main purpose of the paper was to validate a mathematical model and to simulate the process in order to evaluate the rate of absorption. Differential equations were used to describe the process and Matlab and Simulink were used to simulate. The model was validated for one set of experimental data from literature[1].

Base on the model[2] it was studied how the system respond at different changes, such as increasing / decreasing the ratio of liquid and gas phase. The absorption rate was about 90% CO₂.

Keywords: CCS, CO₂, MEA, absorption, simulation, mathematical model

References:
COUPLING OF SOME SIX MEMBERED HETEROCYCLES WITH 4-HYDROXYCUMARIN THROUGH THE HYDRAZINYLIDENE LINK

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The objective of this work is the synthesis and investigation of some novel azo compounds, derived from 4-hydroxycoumarin by coupling with diazotized six membered heterocycles (2-aminopyridine derivatives) in acidic conditions. The recent publications had shown that five membered heterocycles such as diazotated thiazole derivatives coupled with 4-hydroxycoumarin exert very promising pharmacological activities. The idea of including the six membered 2-aminopyridines in the system comes as a result of its biological activities such as anticancer, antiviral, antidote, antithrombotic and anticoagulant. These properties may arise by obtaining more efficient products when combined with the similar activities of 4-hydroxycoumarin.

Keywords: synthesis, 4-hydroxycoumarin derivatives, 2-aminopyridines, antidote, antithrombotic

References:
SUPERCRITICAL CO$_2$ EXTRACTION OF HEAVY METALS FROM AQUA SOLUTION USED CHELATE LIGAND - DITHIZONE

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This study investigated the supercritical CO$_2$ extraction of heavy metals Cu, Pb, and Zn in aqua samples. Combinations of pressure, temperature and modifier conditions for SFE were tested. The extraction was carried out with liquid CO$_2$ at 72 bar and 30°C and with supercritical CO$_2$ at 120 bar and 40°C in a 20 ml stainless steel extractor. Dithizone were used as chelate agent, and methanol as a modifier. After adding the CO$_2$ on the aqueous metal solution, the pressure and temperature were set and the two phase system was stirred for 40 min. After the extraction, the CO$_2$ was released slowly through a restrictor. The remaining aqueous solution in the extractor was analyzed for its metal content by atomic absorption spectroscopy (AAS), determining the recovery of the metal by CO$_2$.

It was found that the extraction efficiency could be improved by using methanol-modified. The highest recoveries obtained were 99.3% for Pb, 94.8% for Zn and 93.0% for Cu, when using supercritical CO$_2$.

**Keywords:** SFE conditions, heavy metals, chelating agent
ARCHAEOOMETRIC STUDIES ON ANCIENT OXIDIC MATERIALS FROM ROMANIA

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Prehistoric pottery, dating from The Middle Bronze age (17th-16th century B.C.) to the Late La Tène (1st century A.D.) and historical roman mortars had been studied by chemical-physical analysis (chemical analyses, X-ray powder diffraction pattern, polarized transmitted light microscopy, thermogravimetric analysis, physical characteristics, Fourier-transformed infrared spectroscopy). The ceramic samples were excavated from an ancient fortification located in present day Șimleu-Silvaniei (NW Romania) and from surrounding areas, while the mortar samples were collected from the ruins of some roman buildings from the ancient capital of the roman province of Dacia, i.e. Sarmizegetusa Ulpia Traiana. The ceramic samples collected from Șimleu-Silvaniei were found to have common origin. In the case of mortar samples, different recipes had been used in order to be obtained.

Keywords: Archaeometry, prehistoric ceramics, ancient roman mortars, Dacia.
STUDYING CE MECHANISM AT THREE-PHASE ELECTRODE, WHERE COUPLED ELECTRON-ION TRANSFER IS COMPLICATED BY COMPLEXATION OF THE TRANSFERRING ION

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An experimental and theoretical study of a complex electrochemical mechanism at three-phase modified electrode, where the coupled electron-ion transfer reaction is complicated by complexation reaction of the transferring ion, has been done. Three-phase electrode system consists of a paraffin impregnated graphite electrode (E), modified with a droplet of a nitrobenzene (O) solution containing neutral redox probe lutetium bis(tetra-tert-butylphtalocyaninato) (LBPC), immersed in an aqueous electrolyte solution (W). LBPC can be oxidized or reduced in one-electron transfer processes at E|O interface to monovalent lipophilic cation or anion, respectively. This causes changes in the electroneutrality of the organic phase promoting transfer of the appropriate ion across O|W interface.

The thermodynamic and kinetic parameters of the saccharinate anion transfer (the most widely used artificial sweetener) across the liquid interface have been studied in details using square-wave voltammetry as an experimental technique and the Gibbs energy, partition coefficient (lipophilicity) and the standard rate constant of this transfer have been determined.

When divalent metal cations (such as Cu2+, Co2+ and Ni2+) are present in the aqueous solution the overall electron-ion transfer reaction at the three-phase electrode is affected by the complexation reactions of the saccharinate ion with these cations. The overall electrochemical mechanism at the three-phase electrode can be described as an CE mechanism. The dissociation of the stable complex M(sacc)2, formed in the aqueous phase, is the chemical step followed by the oxidation of LBPC coupled with the transfer of the free saccharinate anion supplied from the chemical step, as the electrochemical step. The overall mechanism has been studied in details with theoretical simulations using special mathematical approach in the modeling program MATHCAD.

Keywords: three-phase electrodes, square-wave voltammetry, electron-ion transfer reactions, saccharinate anion.
HIGH DENSITY-POLYETHYLENE FOR PHARMACEUTICAL INDUSTRY: THERMAL CHARACTERIZATION

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Polyethylene is widely used thermoplastic polymer with extremely good mechanical properties. Depending on the process condition and molecular parameters (molecular weight, molecular weight distribution, etc.), it can be used as low-(LD-PE), medium- or high-density (HD-PE), as well as high-molecular-weight polyethylene (HMW-PE) for special applications. Polyethylene is used in different fields, such as agriculture, medicine, pharmacy, industry of composite materials, textiles, ballistics, etc. Depending on the application purposes, different characterization methods and techniques are used to determine certain properties of PE: mechanical, electric, oxidative and chemical stability, thermal behavior, etc.

In this study we investigate thermal characteristics of HD-PE aimed for the production of bottles/containers used in pharmaceutical industry. Differential scanning calorimetry (DSC) analysis is applied to determine melting and crystallization behavior of the polymer granulate (containing pigments) under the conditions required for pharmaceutical application. The experiments are conducted at different heating/cooling rates. All runs are carried out in a stream of nitrogen. The thermal stability of samples was investigated by thermogravimetry (TG) under air and nitrogen atmosphere. From the obtained results the changes in the thermal stability of investigated samples in inert and air atmosphere are clearly seen, as a result of different mechanism taking place during degradation.

Keywords: High-density polyethylene, characterization, application

References:
HYDROXYLATED DERIVATIVES OF COENZYME Q\textsubscript{1} AS LIGANDS FOR COMPLEXATION OF TRANSITION METALS

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Coenzymes Q (CoQ) are omnipresent molecules in living systems, which in addition to being members of mitochondrial respiratory chain, possess several other functions of great importance for the cellular metabolism. They are among the most appealing redox active quinone derivatives. In mammals, the predominant homologue is CoQ\textsubscript{10} (ubiquinone).

Unlike CoQ\textsubscript{10} which is lipophilic, its analogue CoQ\textsubscript{1} is much more hydrophilic, because contains only one instead of 10 isoprenoid groups in the tail. The main purpose of using CoQ\textsubscript{1} was to serve as a model for exploring redox properties of CoQ group in aqueous medium.

In an alkaline medium, CoQ\textsubscript{1}s can be hydroxylated at the quinoid ring. The chemical transformations of CoQ\textsubscript{1} in an alkaline medium has been studied by means of cyclic and square-wave voltammetry and it is showed that upon substitution of methoxy groups, hydroxylated derivatives of CoQ\textsubscript{1} are formed. The new hydroxilated derivatives exhibit distinct redox properties compared to the parent compound, as well as a profound complexing activity of transition metal cations such as Fe\textsuperscript{3+} and Co\textsuperscript{2+}.

Besides application of electrochemical techniques, to confirm further the chemical reaction and the structural changes of CoQ\textsubscript{1} in a strong alkaline medium and to investigate the complexing activity of metal cations, a set of spectroscopic experiments has been performed.

\textbf{Keywords}: Coenzyme Q\textsubscript{1}, hydroxylated derivatives of CoQ\textsubscript{1}, cyclic voltammetry, square–wave voltammetry, UV–Vis spectroscopy.
SYNTHESIS AND CHARACTERIZATION OF Co(II) AND Ni(II) COMPLEXES WITH SCHIFF BASES DERIVED FROM SALICYLALDEHYDE

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New complex compounds of Co(II) and Ni(II) with Schiff bases 5-X-salicylideneamine-4H-1,2,4-triazol where (X=H or Br) have been synthesized and characterized. Synthesis of the complexes were performed in two ways: (1) without the presence of triethylamine and water; (2) in the presence of triethylamine and water.

On the basis of infrared and UV-VIS spectroscopic data the synthesized complexes (1) have been formulated as: Diklorobis[2-((4H-1,2,4-triazol-4-ylimino)methyl)phenol]metal(II) where metal = Co(II) or Ni(II). In this case the ligand coordinated to the metal through azomethine group (C=N) and phenolic group, while to complete octahedral structure metal coordinates two chloride ions.

Synthesized complexes (2) may be named as: Diaquabis[2-((4H-1,2,4-triazol-4-ylimino)methyl)phenolato]metal (II). In this case the ligand coordinated to the metal through azomethine group and phenol anion and two water molecules.

The spectroscopic data of the complexes suggests the stoichiometry metal-ligand is 1:2. The results are in accordance with an octahedral environment around the Co(II) and Ni(II) ion.

Keywords: Schiff base, Co and Ni complexes, IR and UV-VIS spectroscopy, X-ray fluorescence.

References:
CHARACTERIZATION OF ELECTRODE PROCESSES BY CYCLIC SQUARE-WAVE VOLTAMMETRY (CSWV)

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A theoretical analysis of reversible and kinetically controlled electrode reactions, as well as electrode processes controlled by kinetics of homogeneous chemical reaction, under conditions of cyclic square-wave voltammetry (CSWV) is presented. The cyclic square-wave voltammetry enables faster and more complete characterization of the electrode processes, comparing with classical square-wave voltammetry. Electron transfer coefficients (α and β), as well as the standard rate constant of a simple electrode reaction Ox + ne⁻ → Red, can be determined from the slopes of linear dependences of cathodic and anodic net peak potentials (Ep) on the logarithm of frequency. Furthermore, the rate constant of follow-up chemical reaction (kf) can be estimated from the linear dependence of anodic to cathodic net peak currents ratio (ΔIp,a/ΔIp,c) on log (f).

The criteria for recognition of electrode mechanisms are given.

Keywords: Cyclic square-wave voltammetry; excitation signal; kinetics; theory.
LOW TEMPERATURE REACTION OF AMORPHOUS SiO$_2$ WITH CALCIUM HYDROXIDE

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The objective of this research was to utilize the diatomite from Rozhden, Kavadarci in order to produce lightweight building materials. The chemical analysis of diatomite shows that it contains over 90 % SiO$_2$, while as reagent was used Ca(OH)$_2$, (product of SIGMA). The diatomite is a suitable material for production of building materials that require minimum preliminary processing (grinding or milling). The mixture containing diatomite and calcium hydroxide ($w = 23 \%$) was homogenized, and in order to achieve the same level of moisture (40 \%) throughout the entire mixture, the mixture was held in hermetically closed space (desiccator) for 24 hours. The formation of the cylindrical probes (10 mm x 15 mm) was performed with cylindrical mold at pressures 10-50 MPa. Further the samples where processed in autoclave for a period of 3 hours, at temperature 130 °C. Upon autoclaving the bulk density of the probes was determined, and it resulted to be in the range 0.79-0.92 g/cm$^3$. The samples were than tested for compressive strength where the results showed strength from 13-20 MPa.

Keywords: hydrothermal reaction, diatomite, calcium hydroxide, mineralogical examination

References:
COMPOSITE ELECTRODES WITH CARBON SUPPORTED Ru-NANOPARTICLES FOR H₂O₂ DETECTION

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A new carbon paste electrode (CPE) incorporating Ru-nanoparticles (RuNP) stabilized on graphite powder was developed for H₂O₂ amperometric detection. Cyclic voltammetric measurements, performed in aqueous phosphate buffer solutions at different potential scan rates, different potential ranges were carried out in order to evaluate the electrochemical behavior of the CPE-RuNP modified electrodes. From amperometric measurements performed at -0.1 V vs. Ag/AgCl, KCl sat, the electrocatalytic efficiency toward H₂O₂ reduction was evaluated and it was found in the range: 28.47 % (CPE) < 94.81 % (CPE-RuNP (2.5:1)) < 118.19 % (CPE-RuNP (2.5:3)) < 152.43 % (CPE-RuNP (2.5:2), recommending the new electrodes as promising sensors for hydrogen peroxide detection.

Keywords: Ru-graphite nanoparticles, H₂O₂ amperometric detection, carbon paste modified electrodes.

References:
MULTI-ELEMENT ANALYSIS OF WINES

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The knowledge of the element composition in wine is very important from toxicological point of view, since it could contains harmful elements, such as Pb, As and Cd, and from nutritional point of view, since wine contains essential elements for the human organism, such as Ca, Cr, Co, K, Se and Zn [1]. The presence of metals (i.e. Al, Zn, Cu, Fe, Pb) in wine is important for efficient alcoholic fermentation and for its sensorial characteristics (flavor, aroma, freshness). The element composition of the wines may be influenced by many factors such as elemental levels in the soil, fertilization practices, as well as processing conditions. Atomic absorption spectroscopy (AAS) is a technique suitable for direct determination of trace elements in wine, one or few elements simultaneously [2]. Electrothermal atomic absorption spectroscopy (ETAAS) technique offers high sensitivity and selectivity for determination of low levels of metals. The most versatile techniques for wine multi-element analysis are inductively coupled plasma - optical emission spectrometry (ICP-OES) and inductively coupled plasma - mass spectrometry (ICP-MS) providing high detection power, high selectivity and sensitivity [3]. However, wine is a complex matrix, containing high ethanol content and other organic compounds and therefore, sample pretreatments, such as dilution and extraction (microextraction techniques with solvents for extraction, single-drop microextraction and dispersive liquid–liquid microextraction) are used in order to extract the metal ions bound in stable complexes. Heating the samples with HNO₃, HClO₄, and H₂SO₄ or mixtures of these acids are commonly used digestion methods, as well as microwave heating digestion in high-pressure digestion vessels using HNO₃, HCl, H₂SO₄, and H₂O₂.

Keywords: elemental composition, wines, AAS, ETAAS, ICP-MS, ICP-OES, digestion.

References
PHOSPHOLE-BASED COMPOUNDS FOR OPTOELECTRONIC APPLICATIONS

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Linear conjugated oligomers and polymers based on aromatic five-membered rings have attracted increasing interest owing to their potential applications for electronic devices. The introduction of phosphole units into conjugated skeletons allows the achievement of interesting opto-electronic properties. Firstly, due to the low aromatic character of this P-ring, derivatives alternating phosphole and thiophene subunits exhibit lower optical band gap than the corresponding oligothiophenes. Secondly, the possibility to perform chemical modifications of the P-atom allows a fine-tuning of the photophysical properties of organophosphorus derivatives. Exploiting this unique property and the coordination ability of the P-atom, access to organophosphorus-containing OLED materials and NLO-phores was achieved. These results show the high potential of organophosphorus derivatives for tailoring of conjugated materials.

References:
HYDROTHERMAL REACTION OF TRIPOLI WITH CALCIUM HYDROXIDE

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In this paper are shown the results of the hydrothermal reaction of tripoli with calcium hydroxide at 110 °C and 130 °C. As raw material was used tripoli as a peculiar sedimentary rock of biogenetic origin from village Suvodol, near Bitola, Republic of Macedonia. Tripoli is lightweight, clay-like rock carrying amorphous silica in the form of fine opal balls. Its bulk density equals 500 to 1200 kg/m\(^3\), porosity 60-70 % and heat conductivity from 0.17 to 0.23 W/m°C. In order to prepare for the hydrothermal reaction of these two components, tripoli initially was crushed and milled in a powder state. A mixture of the 80 % tripoli and 20 % calcium hydroxide was than prepared. The probes were prepared with a cylindrical mold (10 mm x 15 mm) and were pressed on a mechanical press at 2 kN and 10 kN. Further on, the probes were autoclaved at 110 °C and 130 °C for a period of 3 hours. Upon autoclaving the probes were first dried and then their bulk density and compressive strength was determined. The obtained products have shown a bulk density of less than 1200 kg/m\(^3\) and can be classified as light ceramics products. The mineralogical composition of the products has been determined with X-ray analysis.

**Keywords:** hydrothermal reaction, tripoli, calcium hydroxide, compressive strength

**References:**
CHARACTERIZATION OF MACRO AND TRACE ELEMENTS CONTENTS IN EDIBLE OILS WITH APPLICATION OF MICROWAVE DIGESTION AND ICP-MS

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The quality of edible oils regarding their freshness, storability and toxicity can be evaluated by the determination of different macro and trace elements. The quantification of trace elements in oil samples is particularly difficult to perform, as some of them are present at very low concentration levels; therefore, sample preparation is a critical step in the whole analytical procedure. This work presents a quantification approach for elements determination in different types of cold pressed and refined edible oils using inductively coupled plasma -mass spectrometry (ICP-MS) with previously microwave digestion of the oil samples. Studying the content of trace elements, in order to detect tendencies in the samples of the same type of oil, principal components analysis was used. Promising groupings were observed using a model with two principal components.

Keywords: trace elements, edible oils, ICP-MS, principal component analysis.

References:
DEVELOPMENT OF NONENZYMATIC AMPEROMETRIC SENSOR FOR DETECTION OF HYDROGEN PEROXIDE BASED ON MANGANESE(II) CARBONATE THIN FILMS

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The present study contributes to the development of nonenzymatic amperometric sensors for detection of hydrogen peroxide (H\(_2\)O\(_2\)) based on manganese(II) carbonate thin films and has a potential application for glucose detection in biological systems. The thin films are deposited on electroconductive FTO-coated glass substrates using chemical bath deposition method. Thin film chemical composition and structural analysis were studied using XRD and FTIR, and their electrochemical properties and sensitivity towards H\(_2\)O\(_2\) were examined using cyclic voltammetry and amperometry. Thin films with three different thicknesses of 80, 125 and 200 nm were used. The experiments were carried out in a phosphate buffer with \(c(K_2HPO_4/KH_2PO_4) = 0.1 \text{ mol/L and pH } = 7.5\). Wide concentration range of hydrogen peroxide from 5 to 1000 ppm was probed and the most stable electrochemical response was obtained at potential of +0.40 V when using 200 nm thick MnCO\(_3\) film. The calibration plot is associated with a linear regression line and coefficient of \(R^2 = 0.99\).

**Keywords:** hydrogen peroxide (H\(_2\)O\(_2\)), non-enzymatic amperometric sensors, MnCO\(_3\) thin films.

**References**

BAYLIS-HILLMAN REACTIONS CATALYZED BY HEXAMETHYLENETETRAMINE

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The Baylis–Hillman reactions are Carbon-Carbon bond forming reactions, providing multifunctional molecules. Those adduct show a high potency against *P. Falciparum* in vitro (anti-malarial activity). These reactions involve three components: an activated alkene, electrophile and tertiary amine. In general, the rate of the reaction is very slow therefore looking for an efficient catalyst is still challenging effort. Hexamthlenetetramine (HMT)–catalyzed Baylis–Hillman reactions are alternative reactions between an activated alkene and an electrophile. As a very cheap tertiary amine, non hygroscopic and stable reagent of low toxicity, HMT seems to be a catalyst of choice. On the other hand, there are shown improvements in term of reaction time, comparing to reactions developed under the catalytic influence of other tertiary amines. The use of 0.1 equiv or 1.0 equiv of HMT proved to be an efficient catalytically amount for the preparation of desired products under mild reaction conditions and with reasonable reaction times.

**Keywords:** Baylis Hillamn reactions, catalysis, Hexamthlenetetramine.

**References:**
Biocompatible polymers can be used as matrix material for drugs in medicine. In studies, instead of actual active ingredients, they often use model ingredients for easier study. These are usually dyes. I studied chitosan coatings using indigo carmine dye as an incubating agent. The chitosan coatings were created with dip-coating method. The delivery was studied with spectrophotometry in buffer solutions that are close to the pH of human bodily fluids. The chitosan coatings proved to be a good delivery agent in the case of the anionic model substance, because the system had a retard effect and the model substance built up in the coating compared to the incubating solution. The studies showed that it is worth studying the chitosan coatings using real active substance as an incubating agent, also the amount of incubated substance had a correlation with the swelling capabilities of the coatings and this should also be studied in the future.

**Keywords:** chitosan, indigo carmine, drug delivery, pH dependency, model substance

References:
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Posters
PREPARATION AND CHARACTERIZATION OF POLYOXYTHYLATED TERT-BUTYLCALIX[4]ARENE NANOPARTICLES AS PLATFORMS FOR DELIVERY OF CURCUMIN

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The contribution is focused on newly-synthetized octopus-shaped macromolecules, consisting of hydrophobic calix[4]arene core and four arms of hydrophilic poly(ethylene oxide) chains as platform for delivery of hydrophobic agent curcumin. Due to their amphiphilic nature, polyoxyethylated calix(4)arenes (CX[4]PEG) can self-associate in water by forming well-defined spherical nanoparticles. At concentration below the CMC, CX[4]PEG drastically increased curcumin solubility by formation of inclusion complexes with high stability constant (Kc). A significantly higher solubility enhancement of curcumin was observed at concentration exceeding the critical micellar concentration, attributed with additional solubilization of curcumin into the hydrophobic domains of the supramolecular aggregates by non-covalent interactions. The curcumin:CX[4]PEG inclusion complexes as well as curcumin loaded polyoxyethylated tert-buthylic[4]arene supramolecular aggregates were prepared using two methods: heating method and solvent-evaporation method. 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. The in vitro curcumin release profiles from supramolecular CX[4]PEG aggregates were studied under simulated physiological conditions for different incubation periods from 2, 4, 6, 8, 10 and 24 hours. The results showed initial burst release of curcumin, followed by slower drug release. These findings give us a reason to consider polyoxyethylated tert-buthylic[4]arene nanoparticles as promising platforms for drug delivery.

Keywords: curcumin, CMC, CX[4]PEG, nanoparticles, delivery, Kc
STUDY OF NITROGEN POLLUTION IN CROATIA BY MOSS BIOMONITORING AND KJELDAHL METHOD

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During the summer and autumn of 2006 moss samples were collected from 98 sampling sites (85 of which were analysed for N) evenly distributed all over the territory of Croatia. Moss sampling was repeated in 2010 when additional sampling sites were added (in total 121 sampling sites). The most dominant moss species in this study area were Hypnum cupressiforme, Pleurozium schreberi, Homalothecium sericeum, Hylocomium splendens and Brachythecium rutabulum. Kjeldahl method was used to determine the nitrogen content in the samples according to ISO 5663:1984 and EN 25663:1993. Descriptive statistics and distribution maps were prepared. Data obtained from these two surveys were compared, and additional comparison was done with data obtained from similar studies in neighbouring countries and Finland as a clean area. The median value of N content in the samples collected in 2006 is 1.60 % and varies from 0.79 % to 3.16 %. The content of N in samples collected in 2010 ranges between 0.71 % and 2.93 % with the median value of 1.49 %. High contents of N (2.32 % - 3.17 %) were found in the regions of Slavonia, Podravina, Posavina and cities Zagreb and Sisak as a result of agricultural activities, industry and traffic.

Keywords: nitrogen, pollution, moss biomonitoring, Kjeldahl method, Croatia
PREPARATION AND PHOTOCATALYTIC ACTIVITY OF TEMPLATED MESOPOROUS TiO$_2$ THIN FILMS WITH SELECTED POLYMERS

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Homogeneous and crack-free TiO$_2$- based thin films with templated mesoporosity with selected polymers: F127 and PSM02 were prepared by dip coating technique using evaporation-induced self-assembly method. The synthesized mesoporous TiO$_2$ films were characterized using SEM/TEM, BET and XRD techniques. Degradation and/or decolorisation reactions of methylene blue and crystal violet dyes were used to test photocatalytic activity of mesoporous TiO$_2$ films.

Degradation kinetics of methylene blue and crystal violet was investigated in details in broad range of initial concentrations of chosen organic dyes. The kinetic data were correlated with specific surface area, structural properties and thickness of mesoporous TiO$_2$ films, as well as number of reaction cycles.

**Keywords:** Mesoporous TiO$_2$ films, selected polymers: F127 and PSM02, SEM/TEM, BET and XRD techniques.

References:
SYNTHESIS OF FERUM COMPLEXES WITH 3-[2-(THIAZOL-2-YL)HYDRAZINYLIDENE]CHROMAN-2,4-DIONE

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The goal of our experimental work was to synthesised some coumarin complexes. For this aim the ligand firstly was synthesised by coupling reaction of 4-hydroxycoumarin and diazotated 2-aminothiazole. This product was characterised by spectroscopic methods combining spectras: IR, \textsuperscript{1}H-NMR, \textsuperscript{13}C-NMR and MS, as for as x-ray difractometry. The results revelead that the structure of the product is (3E)-3-[2-(thiazol-2-yl)hydrazinylidene]chroman-2,4-dione. The product was tested on the citotoxic activity also and showed very good results.

Furthermore, 3-[2-(thiazol-2-yl)hydrazinylidene]chroman-2,4-dione was used as a ligand due to its convenient configuration to form complexes, in the methanol and in the presence of catalitical amount of triethylamine. To this system, ferum ions from the stock solution of ferum (III) acetate were added. Deep green to brown precipitate was formed as the result of the reaction. The reaction was monitored by TLC and the product was purifed by microcolumn chromatography. This compound can be of special interest for medicinal chemistry for its potential to have prominent anticancer activity.

\textbf{Keywords:} Synthesis, ferro-complexes, hydrazinyliden-chromandiones, anticancer activity

\textbf{References:}
ELECTROCHEMICAL BEHAVIOR OF CAPSAICIN AND ITS ANTI-OXIDATIVE PROPERTIES STUDIED BY MEANS OF CYCLIC VOLTAMMETRY

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The major aim of this work is to study the electrochemical behavior and antioxidative features of the plant derived antioxidant capsaicin. The antioxidant activity and the redox behavior of this compound were investigated by means of cyclic voltammetry at a glassy carbon electrode. Stock solution of capsaicin was prepared in 96% ethanol, and diluted to different concentrations (10, 100, 150, 200, 250, 300 µmol/L). The anodic oxidation behavior of capsaicin and its catalytic (regenerative) effect on the reduction of Ferric to Ferrous ion were investigated in different pH values (3,5; 5,5; 7 and 10) and different scan rates (5 to 100 mV/s). For a comparison of the anti-oxidative properties of capsaicin, voltammetric experiments with vitamin C (100, 200, 300, 400, 500 µmol/L) were also conducted in the same experimental conditions using cyclic voltammetry (CV). Results showed that in acetic buffer with pH=3,6 capsaicin is generating the highest anodic currents \( I_{an} \), and shows well defined voltamograms.

The electrochemical characterization under different conditions is a promising tool to understand the redox behavior of these alkaloids found in Capsicum sp. and only several studies are reported on the electrochemical properties of capsaicin. Therefore, these results can contribute to development of a new method for a rapid estimation of capsaicin and its anti-oxidative properties by fast and simple technique as cyclic voltammetry.

**Key words:** capsaicin, antioxidant, electrochemical, redox potential, voltammetry.

**References:**
Berry fruit and leaf are recognized as potential medicaments which are rich in different phenolic compounds and have been used in folk medicine. In order to evaluate biochemical activity, the cornelian cherry (*Cornus mas* L.) fruit and leaf grown in Southeast Serbia (Vlasina region) were subjected to phenolic analysis. All investigated extracts showed high phenol content from 89.89 to 117.34 mg/g extract dry matter (DM), but different composition of phenolic compounds. All extracts showed significant antioxidant activity (*EC*$_{50}$ from 0.58 to 0.39 mg mL$^{-1}$) and a correlation with the total phenol content. Significant antimicrobial activity was found against Gram-positive and Gram-negative strains, and yeast in all tested extracts.

Cornelian cherry fruit and leaf extracts, rich in phenolic content, with significant antioxidant and antimicrobial activity, can be used as additives in medicinal supplements.

**Keywords:** Cornelian cherry; phenol composition; antioxidant activity; antimicrobial activity.

**References:**
NONCOVALENT INTERACTIONS BETWEEN HEMOGLOBIN AND COMPOUNDS WITH POTENTIAL BIOLOGICAL ACTIVITY

Luana Radu¹, Cristina Bischin¹, Paula Podea¹, Fransisco Carrascoza¹, Radu Silaghi-Dumitrescu¹

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Under conditions of oxidative stress hemoglobin suffers not only autooxidation, but also oxidation to the Fe(IV) state, ferryl. We have previously characterized how ascorbate acts to alleviate this issue, and that it has a particularly high affinity for hemoglobin [1], [2]. Here, we report on experiments aimed to explore to what extent this high affinity is unique among antioxidants. Urate and a number of phenolic compounds are examined to this end via Michaelis-Menten kinetics, establishing particularly low Km values – hence, high affinities. NMR spectra of the antioxidants reveal a selective but multiple-site interaction, which is also explored with docking calculations.

Keywords: hemoglobin, autooxidation, antioxidant, noncovalent interactions.

References:
EVALUATION RADIOCHEMICAL PURITY OF $^{177}$Lu-LABELLED RITUXIMAB CONJUGATES USING HPLC METHOD

Marija Sterjova$^1$, Katarina Smilkov$^1$, Darinka Gorgieva-Ackova$^1$, Angela Carollo$^2$, Marco Chinol$^2$, Emilija Janevik$^1$

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In the field of radiolabelled molecules, Rituximab appear as promising molecules for radiopharmaceutical design, because it can target specifically to antigens in non-Hodgkin lymphoma. In our project, Rituximab was conjugated with DTPA-, DOTA- and 1B4M and prepared in a form of freeze dried kit formulation and labelled with $^{177}$Lu used was 565 MBq (in 5 µL) per kit. The reaction mixture was incubated at 38°C for 1 hour.

The radiochemical purity of the labeled conjugates was determined using SE-HPLC, Column BioSep-SEC-s3000 (300 x 7.5 mm; Phenomenex), with flow rate 1ml/min, isocratic elution – eluent 0.1 M phosphate buffer pH 5.8, UV detection at 220 and 280 nm, analysis time ca. 20 min, sample volume: 20µl.

To around 10 µl of radiolabelled conjugate 10 µl of 10 mM DTPA solution was added in order to bind non-reacted $^{177}$Lu. HPLC analysis was performed 5 min after DTPA addition using UV detection at 220 nm, 280 nm and radiometric detection.

$^{177}$Lu-Rituximab radioimunoconjugates with high radiolabelling yield and average of radiochemical purity (above 94.7%) and specific activity up to 1.5GBq/mg was obtained. With the obtained results we can conclude that $^{177}$Lu- Rituximab radioimunoconjugates can be used for development of the predclinical studies in experimental animal model.

Keywords: HPLC, $^{177}$Lu-Ab-DTPA, $^{77}$Lu-Ab-1B4M, $^{177}$Lu-Ab-DOTA
LOWER RIM FUNCTIONALIZED CALIX[8]ARENES COUPLING TO SILICA SURFACE

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Calixarenic derivatives are of interest for a wide range of applications including chromatography \(^1\), selective metal extraction \(^2\), catalysis \(^3\), etc. This work presents preliminary results in the coupling of calix[8]arenic derivatives to silica surfaces through an APTMS spacer \(^4\) with the purpose of obtaining new materials (Scheme 1.)

![Scheme 1](image)

The obtained products were investigated by means of thermo gravimetric analysis, IR spectroscopy and SEM imaging.

**Keywords:** calix[8]arenes, APTMS, modified silicagel.

**References:**
OPTIMIZATION OF ULTRASONIC EXTRACTION OF POLYPHENOLS FROM GRAPE WASTE USING DESIGN EXPERT SOFTWARE

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After processing of grape into wine certain amounts of polyphenols remain in the grape waste, especially from grape seeds due to fact that their extraction is less efficient compared to other parts of the grape such as grape skin and pulp. The conventional solvent extraction techniques require long extraction time by using certain grade of organic solvents, usually at higher temperature.

The aim of this study was to optimize ultrasound assisted extraction of polyphenols from Vranac grape waste. Ultrasound assisted extraction greatly depends on three independent variables: extraction time, temperature and liquid/solid ratio. Analysis of the experimental design data and calculations of predicted responses were carried out using Design Expert software (Version 7.1.6., Minneapolis, USA). The predicted values of model are in accordance with experimental data obtained under these optimal conditions for this extraction. The ultrasound assisted extraction by RSM of grape waste showed higher extraction yield (14 % increase) and total polyphenolic content (23.15 % increase).

Keywords: Vranac grape waste, ultrasonic extraction method, polyphenolic content, design expert software.

References:
SYNTHESIS OF 4-ARYL/ALKYLAMINOCOUMARINES BY USING MICROWAVE

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4-hydroxycoumarin is a widespread natural product that is used for synthesizing many derivatives which have biological activities. Many theoretical and experimental results have shown that nucleophiles attacks the position 4 of 4-hydroxycoumarin by replacing its OH group. The reaction of 4-hydroxycoumarin with some primary amines under microwave irradiation in solvent free conditions give N-substituted 4-aminocoumarins in good yields. The aim of our work was to synthesize some of the 4-hydroxycoumarin derivatives and to prove that using a domestic microwave we could cause nucleophilic substitution on position 4 of 4-hydroxycoumarin if primary amines are used as nucleophile substances. The main advantages of this method are: dramatically shorted reaction time and considerably good yields. The reaction and the obtained product were monitored by determination of the melting points, solubility table of products and also thin layer chromatography.

Keywords: 4-hydroxycoumarin, 4-aminocoumarins, nucleophilic substitution, microwave irradiation

References:
EFFECT OF SELECTIVE REMOVAL OF GRAPEVINE LEAVES OF CABERNET SAUVIGNON POLYPHENOLIC CONTENT

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The selective removal of grapevine leaves (defoliation) around berry clusters can improve the quality of ripening fruits by influencing the phenolic content at harvest. We removed the basal leaves from Cabernet Sauvignon *Vitis vinifera* L. grapevine variety in Serbia (Rajački vineyard region). Balkan region has modern vineyards, 80 per cent of which are planted with red wine grapes including Cabernet Sauvignon and Merlot. Considering the economic importance of winemaking, it is necessary to find tools for completing the quality of their red wines. According to the results, early defoliation allowed achieving highest content of polyphenols in the berry skin and highest antioxidant activity, while late defoliation made to lower content of polyphenols and antioxidant activity compared to control (untreated) vine. Thus, the best period for defoliation of the Cabernet Sauvignon grapevine variety was after full blooming, in order to increase polyphenolic skin content and antioxidant activity.

Keywords: Cabernet Sauvignon, defoliation, polyphenols, antioxidant activity.

References:
MICROWAVE-ASSISTED ORGANIC SYNTHESIS OF SOME N-ALKYL SUBSTITUTED ISATIN 3-THIOCARBOHYDRAZONES

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Isatin (1H-indole-2,3-dione) is a precursor for a large number of pharmacologically active compounds with significant importance in medicinal chemistry. N-substituted isatins have been frequently used for preparation of a wide variety of heterocyclic compounds. In this work, thiocarbohydrazones of N-alkyl substituted isatin were synthesized to develop more effective small molecules with potential antiproliferative activity. Microwave-assisted organic synthesis (MAOS) has been shown to be an invaluable tool for drug discovery applications since it often dramatically reduces reaction times. Herein, the synthesis of N-methylisatin-3-thiocarbohydrazone (N-Me-IsTCH) and N-ethylisatin-3-thiocarbohydrazone (N-Et-IsTCH), which were obtained via reaction of carbonyl-amine condensation under microwave irradiation and traditional conductive heating methods, are presented. The microwave irradiation as a simple and efficient technique offers many advantages over conventional heating, such as decreasing reaction time, increasing yields and taking minimum solvent or almost solvent-free conditions, which uploads the motto of green chemistry. The synthesized compounds were characterized and confirmed by spectroscopic analysis data (FT-IR, 1H-NMR, 13C-NMR).

Keywords: N-methylisatin-3-thiocarbohydrazone, N-ethylisatin-3-thiocarbohydrazone, microwave-assisted organic synthesis (MAOS).

References:
DETERMINATION OF OXIDATIVE STATUS IN EDTA PLASMA OF HEMODIALYSIS PATIENTS BY PEROX ASSAY

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²Center for Hemodialysis, Stip, R. Macedonia

Patients with end stage renal disease undergoing regular hemodialysis very often suffer from oxidative stress, which is defined as a state where the production of reactive oxygen species exceeds the capacity of the antioxidant defense systems in the cells and tissues. It has been observed that the free radical induced lipid peroxidation can further lead to a significant tissue damage, which plays role in the pathogenesis of various co-morbidities in the hemodialysis patients.

The aim of this study was to determine the plasma levels of total hydroperoxides in hemodialysis patients before the single hemodialysis session (N=13) in comparison with healthy persons (N=38), using an in-house PerOx assay, as an indication and quantification of the plasma oxidative status/oxidative stress. The determination of plasma hydroperoxides was performed by their reaction with horseradish peroxidase, followed by conversion of tetramethylbenzidine (TMB) into a colored product. Commercial standards with known concentrations of H₂O₂ in plasma matrix were used for calibration of the assay.

The results from the PerOx assay have shown that hemodialysis patients have significantly higher concentrations of plasma hydroperoxides (287±84 CARR U) than healthy subjects (238±65 CARR U) p<0.05 (one CARR U corresponds to 0.08 mg/100mL H₂O₂). These results indicate that the PerOx assay reflects an increased oxidative stress which is related to the end stage renal disease and chronic hemodialysis.

Further analyses are needed to establish the value of this assay with regards of the effects of the single hemodialysis session, the possible antioxidant supplementation and the comorbidities in the hemodialysis patients.

Keywords: Oxidative status, Hemodialysis patients, PerOx assay
GEOCHEMICAL ANALYSIS OF TRACE METALS: SOKOBANJA LIMESTONE

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Limestones are the most widespread carbonate rocks. Recognized as readily react with cold HCl. Structure of them depends on the way of creation. Chemical limestones are crystalline structures, limestone incurred in processing the previous carbonate rocks are clastic structure and organogenic limestones have organogenic structures and the name given to the type of fossils. Sokobanja valley by its position, geological and ecological characteristics of the complex territorial system, whose parts characterized by mutual dependence, is very interesting for geochemical investigations. The interaction of the above elements has led to the formation of separate regional structures of the studied area dominated by two complementary macro-region - the Carpathian and Balkan Serbia. The geospatial unit covers the central and eastern part of Serbia, and the space between the Timok basin on one side and the Morava basin on the other. Samples were subjected to fractional analysis. First, they were treated with acetate buffer and then with cold HCl. For each fraction was determined by the concentration of trace metals- inductively coupled plasma optical emission spectrometry (ICP-OES).

Keywords: Limestone, Sokobanja valley, trace metals, ICP-OES.

References:
BAYLIS-HILLMAN REACTIONS CATALYZED BY HEZAMETHYLENETETRAMINE

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The Baylis–Hillman reactions are Carbon-Carbon bond forming reactions, providing multifunctional molecules. Those adduct show a high potency against \textit{P. Falciparum} in vitro (anti-malarial activity). These reactions involve three components: an activated alkene, electrophile and tertiary amine. In general, the rate of the reaction is very slow therefore looking for an efficient catalyst is still challenging effort. Hexamthylenetetramine (HMT)–catalyzed Baylis–Hillman reactions are alternative reactions between an activated alkene and an electrophile. As a very cheap tertiary amine, non hygroscopic and stable reagent of low toxicity, HMT seems to be a catalyst of choice. On the other hand, there are shown improvements in term of reaction time, comparing to reactions developed under the catalytic influence of other tertiary amines. The use of 0.1 equiv or 1.0 equiv of HMT proved to be an efficient catalytically amount for the preparation of desired products under mild reaction conditions and with reasonable reaction times.

Keywords: Baylis Hillmann reactions, catalysis, Hexamthylenetetramine.

References:
MECHANISTIC INVESTIGATIONS OF UNDESIRED PROOXIDANT REACTIONS IN COMPOUNDS AND NATURAL EXTRACTS WITH ANTIOXIDANT ACTIVITY

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The goal of our study is to investigate to what extent the generally-accepted antioxidant activity of plant extracts, or indeed of synthetic concentrated antioxidant preparations, can develop prooxidant activity. The use of anti-oxidants provides clues about the involvement of free radicals, superoxide and peroxide in such processes. Current debates about the use of antioxidants (including high doses) in anticancer treatments are among the reasons why this line appears worthwhile pursuing.

Fig. 1. Interaction between oxyhemoglobin, PBS, Chelidonium majus, catalase and superoxide dismutase

Keywords: hemoglobin, prooxidant activity, Chelidonium majus.

References: