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BOOK OF ABSTRACTS

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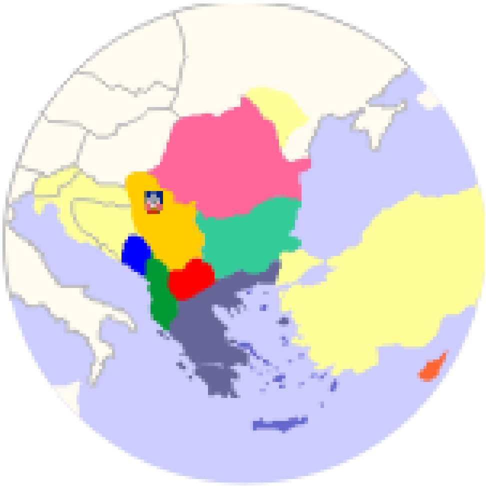

Chemistry of Cluster Active Sites of Oxidoreductases Drawing a Lesson from the Brilliant Functions of the Enzymes for our Future Sustainable Society

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Metalloenzymes are essential for all organisms on Earth, and their metal-incorporating active centers regulate highly efficient and selective chemical transformations under mild conditions. The recent structural studies of reductases and Photosystem II have revealed unusual transition metal clusters at the active sites. They show remarkable activities, as exemplified by CO-dehydrogenases generating protons and electrons from CO and water, hydrogenases converting dihydrogen into protons and electrons reversibly, nitrogenases catalyzing the reduction of dinitrogen into ammonia, and the oxygen-evolving center of Photosystem II splitting water into dioxygen, proton, and electron. These enzymatic functions could provide us with clues to the realization of a sustainable society. An important and pressing mission of chemists is to synthesize model active sites in vitro and to elucidate the mechanisms of biological functions.

This presentation begins with an overview of the intriguing functions of the cluster active centers of these oxidoreductases, which are regarded as a key to realizing a sustainable society. Then our recent study on the chemical synthesis of Fe/S and Fe/Mo/S clusters modeling P-cluster and FeMo-co of nitrogenase and on the synthesis of Mn/O(OH) clusters modeling the oxygen-evolving center of photosystem II are presented. These model clusters have been isolated from the reactions of $Fe\{N(SiMe_3)_2\}_2$ with bulky thiol and S_8 in toluene, or from the reactions of $Mn\{N(SiMe_3)_2\}_2$ with bulky alcohol/silanol in toluene under the presence of a minimum amount of H_2O or O_2.

The study on the bio-inspired activation of H_2, H_2O, CO, and N_2 will promote development of advanced science-based innovation and will make significant contributions to realizing a sustainable society.

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New bent-core liquid crystals, mesophases and structure-property relationship

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Introduction

The first liquid crystals were isolated in 1888 by professor Reinitzer who was studying the development of the plants. After many purifications the compounds were turbid after melting and clear fluids could be obtained in further heating to a higher temperature. He asked the German physicist Lehman to investigate the compounds and after two years he could establish, that there are intermediate states between the solid and fluid state. So the states were called mesophases. The first compounds were cholesterin derivatives, especially, cholesteryl benzoate, so this phase was called cholesteryl phase. Because these derivatives were chiral compounds, the observed mesophase was the chiral variant of the nematic phase. Later many two aromatic ring containing compounds were prepared in Halle by professor Vorlaender [1], more and more mesophases were described. The nematic phase has no layer structure, the directores of the molecules (long axis) are oriented almost paralell to each other, but their central parts are shifted. The longer terminal alkyl chain containing compounds show higher orientation, the consisting molecules can form layer structures, but there is no positional ordering in the layers. The mesophases are established by polarization optical micsroscopy, differencial scanning calorimetry shows the enthalpy changes between the mesophases, and layers are characterized by X-ray diffraction [2, 3]. During the sixties and seventies of the 20th century it turned out, that the liquid crystalline molecules can be addressed by the electric field, and a fast development occured in the display techniques. Now we can buy high definition TV sets with large screens, but in everyday life we use mobile phones, displays in science even in our laboratories. Not only displays are important, but now actuators are also planned which are addressed by the magnetic field. The polymers of liquid crystals can serve in data storage.

Bent-core liquid crystals

Until now we have been dealing with two or three aromatic ring containg linear-shaped compounds which made a revolution in the display technique. In 1996 on the International Liquid Crystal Conference Japanese authors presented the BANANA-shaped or BENT-core liquid crystals, which results opened a new subfield of the liquid crystal research [4].

If one add two mesogenic units to a central part and a kink is built in the molecular structure, than one can have a bent in the core of the molecule. The first bananas contained five aromatic rings, the connecting groups were ester and azomethine groups. Four new mesophases were described on the first bananas, now we know eight new phases. The main goal of this research is that the chiral mesophases appeared in the non-chiral molecules. The molecular structure is asimmetrical and by the chirality transfer the system of the ordered molecules become macroscopically chiral. In this way, the system behaves as the consitutent molecules were chiral.

The ferroelectric switching, which was observed on linear-shaped molecules containing chiral group(s), was detected on some non-chiral bent core materials. The molecules favour to form layered structures. Due to the polar packing the individual layers have a polar vector pointing in the same direction. In the lecture it will be showed how many orientations of the layers are possible to form homogenously chiral and heterogenously chiral systems. Some molecules can also have nematic phase, but this phase is also quite different from the nematic phase of the linear-shaped compounds. It was predicted, that the nematic phase of the bent core materials can be optically biaxial, inspite of the linear-shaped compounds which can have only uniaxial phases. A detailed summary of the new results are reviewed in ref. 6.

Little changes in the chemical structure can induce the appearance of some mesophases or suppress them.

New phenomena were observed in these new compounds. The giant flexoelectric behavior [7], or the clusters in the nematic phases [8] should be mentioned here.

Acknowledgement: *The author is thankful to Prof. A. Jákli and Prof. G. Galli for helpful discussions, to Hungarian Research Fund OTKA K-81250 for the financial support, further to the Serbian Hungarian bilateral collaboration, and to the Serbian Chemical Society.*

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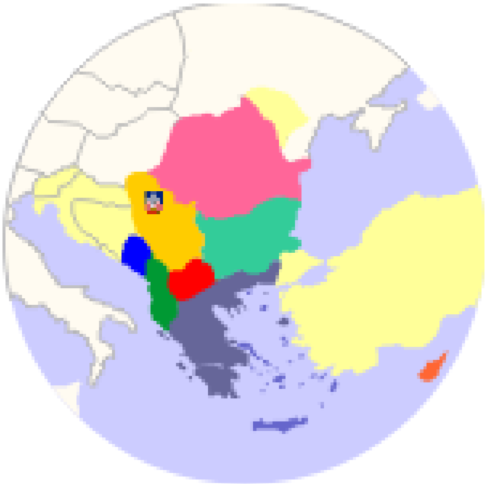
Invited Lectures



Anticancer properties of nanostructured materials functionalized with metal complexes or natural products

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Current cancer treatment is multidisciplinary and includes hormonotherapy, radiotherapy and chemotherapy. The latter is the treatment of cancer with an antineoplasic drug or a combination of anticancer drugs to stop or decrease the uncontrolled growing of cancer cells. In this context, the discovery of cisplatin and other metal analogues was of crucial importance for the treatment of many cancer patients. The successful use of these compounds in chemotherapeutic treatments for humans was an inflection point for the development of novel anticancer agents [1].

However, the limitations associated to anticancer chemotherapy in humans; such as side-effects, difficulties in the preparation of water-friendly formulations and problems with the recurrence of tumors associated to a multidrug resistance; shifted the interest of the scientific community to test the use of novel scaffolds, encapsulators or carrier vehicles as vectors for the delivery of the anticancer agents in local areas in order to improve the applicability in humans [1].

For these reasons, our group became interested in the use of nanostructured porous materials (such as MCM-41, SBA-15, nanocrystals of hydroxyapatite and alumina nanoparticles among others) which have been studied in a wide variety of biological applications, being able to locally deliver drugs for the treatment of bone pathologies [2]. Thus, a wide variety of nanostructured materials functionalized with metal complexes has recently been prepared by our group. These novel systems have been tested *in vitro* against different cancer cell lines showing that they may be potentially useful as adjuvant agents for avoiding the recurrence of bone tumours [3].

The deep study of these novel materials led us to investigate the functionalization of similar systems with natural products with potential application as anticancer drugs, due to their interesting antineoplasic properties [4].

The latest results of our group, including the use of metal-based drugs and natural products as anticancer agents, will be discussed.

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Visualization of Biological Processes Using Responsive MRI Contrast Agents

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Max Planck Institute for Biological Cybernetics, Physiology of Cognitive Processes,
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Magnetic resonance imaging (MRI) has evolved into a powerful tool in modern biomedical research. Its signal specificity can be further improved using contrast agents and their application has largely contributed to the MRI development.

The aim of our group is to develop new measurement techniques that would enable visualization of neuronal activity and better understanding of brain function by using responsive (or 'smart') agents. These are biochemical markers that alter their MR signal upon a certain biochemical event due to changes in their microenvironment.

Calcium is an excellent marker tightly linked to brain activation, which has typically been the preferred target for a number of optical imaging methods. To accomplish our goals, we synthesize and study smart MRI contrast agents, complexes that respond to differing concentrations of endogenous Ca^{2+} by altering their magnetic properties.

Over the past years we have reported a number of Gd^{3+} chelates linked to modified Ca^{2+} chelators that act as smart MRI contrast agents.[1] Some of the agents exhibited remarkable sensitivity towards Ca^{2+}, and their physicochemical characteristics were found to be superior to any other previously described Ca^{2+}-sensitive MRI agents.[2]

In parallel, we developed a series of fluorine-containing complexes with a range of paramagnetic and diamagnetic ions. They exhibit high proton longitudinal relaxivities while displaying an increase in ^{19}F relaxation rates which are favorable for ^{19}F MRI experiments.[3] Subsequently, the complexes that contain a Ca^{2+} chelator in between the paramagnetic and fluorine-containing moieties are prepared and they are capable of reporting the changes in Ca^{2+} concentrations simultaneously by ^{1}H and ^{19}F MRI. Extensive studies revealed mechanisms which underly the intramolecular changes triggered by Ca^{2+}, and are responsible for the alternation of the MRI signals at both frequencies.[4]

A new generation of dual-frequency probes suitable for both ^{1}H and ^{19}F MRI opens novel perspectives for successful assessment of Ca^{2+} in living organisms. The ability to observe its concentration changes in a non-invasive fashion would be of paramount importance for MRI methodology advancements and biomedical research in general.

The presentation will give a brief overview of smart MRI contrast agents recently studied and reported by our group.

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Mediterranean diet as a symbol of health and economic development

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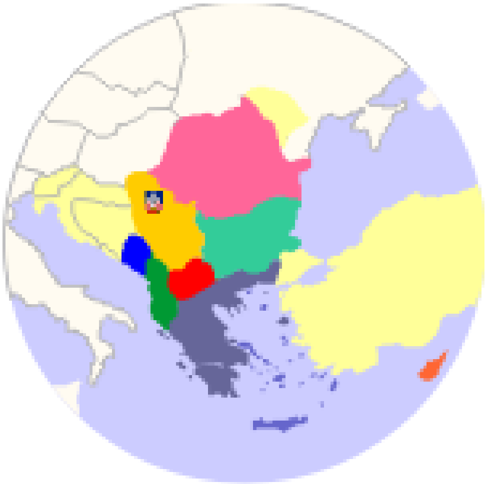
National Centre of Scientific Research "DEMOKRITOS“

In November 10 of 2010 UNESCO approved the Mediterranean Diet as a part of the Intangible Cultural Heritage of the Humanity. The proposal was submitted by Italy, Spain, Greece and Marocco two years before. According to the proposal every country has to propose a town representative of the Mediterranean Diet. So Greece propose Koroni which is a beautiful city in the south of Peloponese, Italy suggested Silento. Spain the town Soria and Marocco the city of Shefsauen. Also every country has to propose a dish representative of the country and the Mediterranean Diet so Greece suggested the greek salad ,Italy spaggeti Cambreze.Spain paelia,and Marocco the tatzin maroccane.As was emphasized in the report of UNESCO that despite the historic,cultural and religious differences the four countries share three common agricultural products: these are the olive oil,the grapes and the wheat.The golden trilogy as was refered from UNESCO is what brings together the people of the Mediterranean countries in cultural, societal and other every day events.

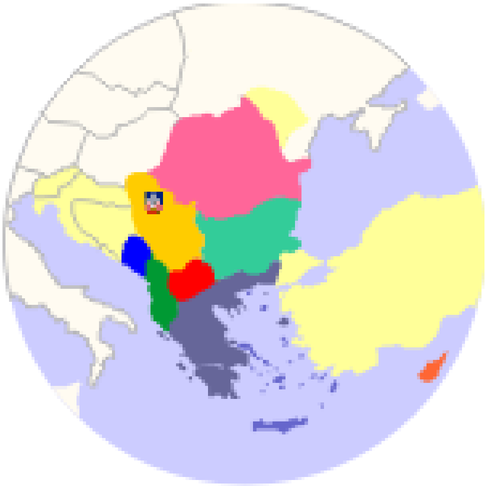
The Mediterranean Diet as a symbol of health,wellbeing,and longliving must be adopted mainly in the Mediterranean countries since the modern way of living changed our diet habits to fast foods and ready made dinners (TV dinners).The pyramid of the Mediterranean diet is well known and consists mainly on fruits and vegetables,salads , legumes,seeds ,olive oil and other similar products of the Mediterranean land.Sweets and red meat must be avoided, it is allowed a limited quantity of wine and a lot of mild exercise (walking).

The Mediterranean Diet that is based on products of the Mediterranean soil when are being consumed help also the economy of the country and combined with the national cuisine they assist in the increase of tourism in the mediterranean area.

Contributions



1. Breakthrough Science



Synthesis

O 01 BS-Sy

Double *N*- and *S*-arylation for synthesis of azepine and thiepine derivatives

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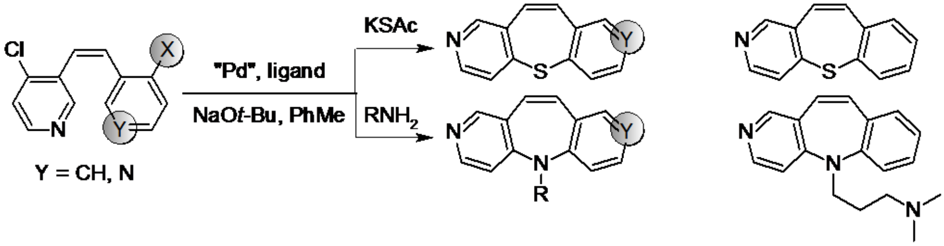
Azepines and thiepines, compounds with seven-membered nitrogen- and sulfur-containing rings, can show significant pharmaceutical activity. Derivatives of 5*H*-dibenz[*b*,*f*]azepine are important precursors in the synthesis of several of biologically active compounds, with antiepileptic and antidepressant activity (imipramine). Antipsychotic drug Zotepine contains a dibenzothiepine moiety. Use of di-halo compounds for double palladium-catalyzed *N*-arylation reaction is a well established methodology for the formation of heterocyclic skeletons: carbazoles, thienopyrroles, indoles and phenazines, but very few examples of the double palladium-catalyzed *N*-arylation reaction for the synthesis of the azepine ring system are known [1]. *Additionally*, only one approach for the synthesis of thiepines involves the palladium-catalyzed reaction [2].

Herein we report the synthesis of new 5*H*-piridobenzazepine and 5*H*-dipirydoazepine compounds using the palladium-catalyzed amination-cyclization as a key step. By choosing an appropriate combination of ligands and reactants under standardized reaction conditions, *N*- and *S*-containing tricyclic products can be prepared in one step from the appropriate *ortho*-halogensupstituted *Z*-stilbenes. Various stilbenes were subjected to Pd-catalyzed reactions with amines at 100 °C for 24 h and the desired azepines were obtained in fairly good yields. In our approach for the preparation of thiepines, we used potassium thioacetate as a source of sulfur for C-S bond formation. We explored microwave-heated double palladium-catalyzed C-S bond formations. Reaction time was significantly reduced and the yields of the desired compounds obtained using the microwave-accelerated protocol were higher.



Acknowledgment: *This research was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (grant no. 172008) and NATO's Public Diplomacy Division in the framework of Science for Peace project SfP983638.*

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O 02 BS-Sy

Development of a sinthetic route to corialstonidine

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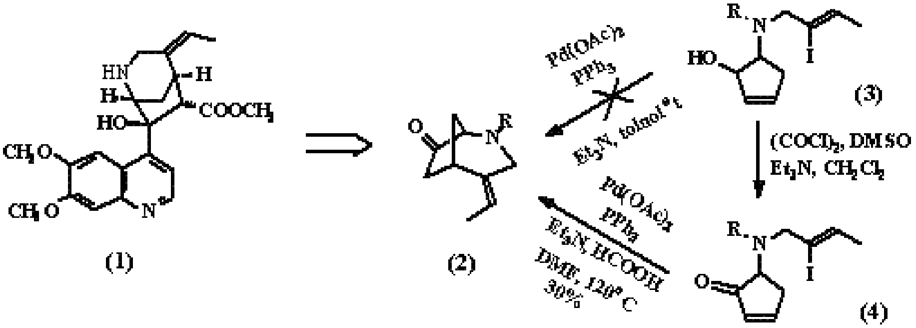
Alkaloids with bicyclic skeleton are present in many plants used in traditional medicine to treat malaria, fever, arrhythmia and other diseases[1]. Corialstonidin **(1)** is an alkaloid isolated from *Alstonia coriacea* showing significant antimalarial activity against *P. falciparum*[2]. In order to develop a synthetic routes to corialstonidine, cyclisations reactions of allylic alcohols promoted by palladium catalysts were studied. Although the cyclization process was successfully developed on a model system furnishing a product with desired bicyclic skeleton[3], intramolecular Heck reaction of cyclic allyl alcohol **(3)** did not produce bicyclic ketone **(2)**, a key intermediate in the synthesis of natural products. For this reason, allyl alcohol was subjected to oxidation to afford **(4)**, which was then cyclised under reductive conditions producing azabicyclo[3.2.1] octane in 30 % yield (scheme 1).



Scheme 1

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O 03 BS-Sy

Is the reduction of gold(III) ''culprit'' for its biological activity?

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Substitution as initial step in the reaction between gold(III) and thiols/thioethers

Even though the gold(III) complexes show outstanding cytotoxic properties on different cancer lines, mechanism of the reaction appears as unknown. Since 1970 it was a doubt does substitution proceed in the reaction of gold(III) and sulfur donor nucleophiles, or the reduction occurs as a single step [1].

In order to investigate a detailed study in this field, we employed four complexes $[Au(terpy)Cl]Cl_2$ (terpy = 2,2':6'2"-terpyridine), $[Au(bpma)Cl]Cl_2$ (bpma = bis(pyridyl-methyl)amine), $[Au(dien)Cl]Cl_2$ (dien = diethylenetriamine) and $KAuCl_4$, three nucleophiles (L-Methionine, L-Cysteine, Glutathione) and four different techniques (UV-Vis spectrophotometry, stopped-flow spectrophotometry, proton NMR, cyclic voltammetry).

Using the stopped-flow technique it has been found that the reduction proceeds as a subsequent step with initial substitution, while cyclic voltammetry was useful to detect an intermediate gold(I) formation. Investigated complexes show that the chelating effect of coordinated ligands make an influence on stability of gold(III) center under the biologic relevant conditions. Going from dien through bpma to terpy complex substitution step was easier detectable prior to reduction. This behavior was expected due to influence of stabilization caused by increasing the π-donor ability, what makes substitution faster.

The obtained results suggest the reaction mechanism of the studied systems and can impose the explanation why the gold(III) center shows a promising biologic activity even though the reduction is present *in vivo.*[2]

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O 15 BS-Sy

New derivatives of hydantoin as potential antiproliferative agents

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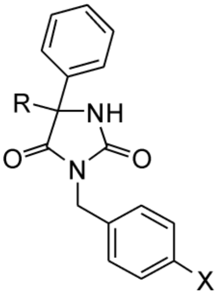
Two series of hydantoins: 3-(4-substituted benzyl)- 5,5-diphenyl- and 3-(4-substituted benzyl)-5-ethyl-5-phenyl-hydantoins (Fig. 1) were synthesized and characterized by FTIR, ^{1}H and ^{13}C NMR spectroscopy. Compounds **2a**, **2c** and **2g** were additionally characterized by single-crystal X-ray diffraction. The *in vitro* antiproliferative activity of the investigated compounds was evaluated against the cells of two human cancer cell lines: HCT-116 (colon cancer) and MDA-MB-231 (breast cancer). In general, all compounds show superior antiproliferative activity against MDA-MB-231 than against HCT-116 cell line, whereby those in series 1 possess higher potencies than the compounds in series 2.



Compound	R	X	Compound	R	X
1a	C_6H_5	H	**2a**	C_2H_5	H
1b	C_6H_5	CH_3	**2b**	C_2H_5	CH_3
1c	C_6H_5	$C(CH_3)_3$	**2c**	C_2H_5	OCH_3
1d	C_6H_5	OCH_3	**2d**	C_2H_5	Cl
1e	C_6H_5	Cl	**2e**	C_2H_5	Br
1f	C_6H_5	Br	**2f**	C_2H_5	NO_2
1g	C_6H_5	NO_2	**2g**	C_2H_5	CN
1h	C_6H_5	CN			

Figure 1. *Chemical structures of the investigated compounds*

X-ray analysis revealed that derivative **2a** is triclinic with space group *P*–1¸ while derivatives **2c** and **2g** crystallize as monoclinic in the space group $P2_1/c$. The molecular structures are as expected with normal bond distances and angles. Crystal packings are governed by hydrogen N–H···O bonds between neighboring molecules. In **2a,** hydrogen bonds make $R^2_2(8)$ centrosymmetric dimmers along *c*–axis. In other two compounds, N–H···O bonds between neighboring molecules built pseudo-double layers. These layers are connected by only van der Wals forces.

BS-Sy P01

Complex formation reactions of two sterically hindered Pt(II) complexes with some sulfur and nitrogen bonding ligands

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Presently, platinum drugs are playing a major role within established medical treatments of cancer. The clinical success of cisplatin has produced an interest in synthesis of structurally different platinum metallodrugs that might exhibit better cytotoxic properties, hopefully accompanied by different antitumor specificities.[1]

Complex compounds of Pt(II) with inert tridentate nitrogen-donor ligands such as diethylenetriamine (dien), *bis*-(2-pyridylmethyl)amine (bpma), 2,2′:6′,2′′-terpyridine (*terpy*), 2,6-bis[(1,3-di-*tert*-butylimidazolin-2-imino)methyl]pyridine (TL^{tBu}) and tripyridinedimethane (tpdm) are very useful models for studying the ligand substitution reactions of square-planar complexes. These complexes are monofunctional and they do not show antitumor activity, but they are very useful for the study of the first step of the reaction with biologically important molecules.[2]

As an extension of earlier work,[3] here we reported the results of substitution reactions of monofunctional Pt(II) complexes: $[(TL^{tBu})PtCl]^+$ and $[Pt(tpdm)Cl]^+$ where TL^{tBu} = 2,6-Bis[(1,3-di-*tert*-butylimidazolin-2-imino)methyl]pyridine and tpdm = terpyridinedimethane with N-bonding nucleophiles: L-histidine (L-His), inosine (Ino), inosine-5’-monophosphate (5’-IMP) and guanosine-5’-monophosphate (5’-GMP) and S-bonding nucleophiles: *S*-methyl-L-cysteine (*S*-Met-L-Cys), L-cysteine (L-Cys), glutathione (GSH) and L-methionine (L-Met). All reactions were studied in aqueous 0.1 M $NaClO_4$, in the presence of 10 mM NaCl, at three different temperatures (288, 298 and 308 K). The reactions were followed by using UV-VIS spectrophotometry under the *pseudo*-first-order conditions with a large excess of nucleophiles. According to the obtained results could be concluded that the complexes with tpdm ligand react faster than the complexes with TL^{tBu} ligand. The lower reactivity of the complexes with TL^{tBu} ligand is the result of the bulkiness of the *tert*-butyl-groups. In addition, this complex contains bulky imidazolin-2-imine moieties with a strong electron-donating capacity. The order of reactivity of studied ligands is in agreement with their electronic and structural characteristics.

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BS-Sy P02

Synthesis of *N,N*-diethyl-1-ferrocenyl-3-thiabutanamine and its application in Suzuki-Miyaura cross coupling

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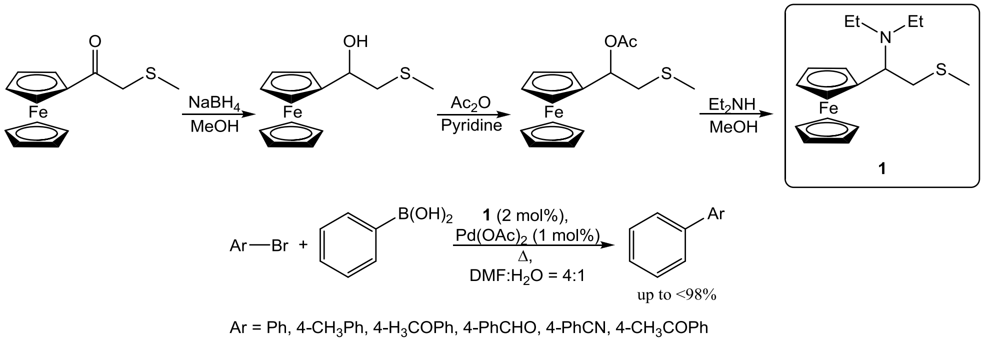
Increasing interest in palladium catalyzed cross-coupling processes urges synthesis (and utilization in this field) of diverse organic compounds - suitable ligands for complexation with the corresponding metal ions. Among these, compounds capable of making chelates are of a particular interest. The Suzuki reaction is one of the most useful cross-coupling reactions, applicable on both laboratory and industrial scales [1]. In this work we wish to report on synthesis of *N,N*-diethyl-1-ferrocenyl-3-thiabutanamine (**1**) and utilization of its complex with the palladium(II) ion in Suzuki-Miyaura reaction (see the scheme bellow).



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BS-Sy P03

Synthesis and characterization of a gold(III) complex with isoamyl ester of (*S,S*)-ethylenediamine-*N,N'*-di-2-propionic acid

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After the great success of cisplatin in cancer treatment, special attention was devoted to evaluation of gold(III) complexes as potential antitumor agents due to the fact that both platinum(II) and gold(III) ions possess the same d^8 electronic configuration and form square-planar complexes [1].

Recently, a few gold(III) complexes with R_2edda-type ligands, esters of (*S*,*S*)-ethylenediamine-*N,N'*-di-2-(3-cyclohexyl)propanoic acid, were found to be very active against K562 cell line [2].

Novel ligand precursor, *O,O'*-diisoamyl-(*S,S*)-ethylenediamine-*N,N'*-di-2-propanoate dihydrochloride, and the corresponding gold(III) complex, $[AuCl_2\{(S,S)\text{-}(i\text{-}Am)_2eddip\}]PF_6$, were synhesized and characterized by IR, NMR spectroscopy, mass spectrometry and by elemental analysis.

IR spectrum of the complex shows strong absorption stretchng ν(C=O) band around 1733 cm^{-1} (ligand precursor: 1739 cm^{-1}), which indicates that cordination of the carboxylic oxygen to the metal center is excluded. The change of values of asymmetric C−N vibrations from 803 cm^{-1} for ligand precursor to 847 cm^{-1} for complex suggests that the ligand coordinates *via* nitrogen atoms. In ^{1}H NMR spectrum chemical shifts of protons from ethylenediamine moiety were found upfield 0.5 ppm in comparison to the ligand precursor and this indicates coordination of the ligand through nitrogen atoms. In ^{13}C NMR spectrum of $[AuCl_2\{(S,S)\text{-}(i\text{-}Am)_2eddip\}]PF_6$, isoamyl carbon atoms show resonances similar to those observed for the ligand precursor, as well as for the carbon atoms from the ester function.

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BS-Sy P04

Synthesis and structural characterization of four new Pd complexes with *N,N*-donor ligands

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Metal complexes have been examinated as anticancer drug for a long time. Because of well known side effects of cisplatin and other second-generation platinum drugs, research is moved to the synthesis of new compounds with another metal ion. Based on the similarities of coordination geometry and thermodynamic parameters of the palladium(II) complexes with platinum(II) complexes a lot of these compounds have been synthesized and tested so far. Palladium(II), as a soft Lewis acid, has the ability to form stable chelating rings with N,N; N,S or N,O donors.[1]

Having in mind very good cytotoxic activity of N,N donor ligands, n-alkyl esters of (*S,S*)-ethylenediamine-*N,N'*-di-2-(3-cyclohexyl)propanoic acid [2], four new complexes of palladium(II) were obtained by the reaction of $K_2[PdCl_4]$ and equimolar amount of corresponding ligand. The complexes were characterized by ^1H and ^{13}C NMR, IR and mass spectroscopy. The proposed scheme is given in Figure 1.

Cytotoxic potential of these complexes is under current investigation. Due to very good activity of the ligands themselves and enhanced kinetical activity of palladium(II), significant activity of prepared complexes could be expected.

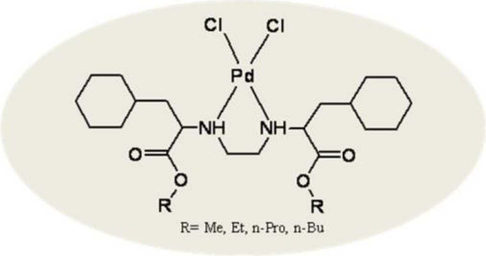

Figure 1. *Stucture of Pd(II) complexes with n-alkyl esters of (S,S)-ethylenediamine-N,N'-di-2-(3-cyclohexyl)propanoic acid.*

Acknowledgement: *This work was supported by the Ministry of Science of the Republic of Serbia, grant numbers 172035*

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BS-Sy P05

Synthesis and cytotoxic investigation of new Pt(II) and Pt(IV) complexes with thiacyclopentane- and thiacylohexanespiro-5’-hydantoins

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Two Pt(II) and two Pt(IV) complexes with thiacyclopentanespiro-5’-hydantoin and thiacyclohexanespiro-5’-hydantoin were synthesized. The new complexes were characterized by elemental analysis, IR, ^{1}NMR, ^{13}C NMR spectra in solid state and in the solution. DFT calculations at the B3LYP/LanL2DZ level of theory are very useful in prediction of the structures and spectroscopic behavior of the metal complexes. Some DFT calculations about geometry optimization of new Pt(II) and Pt(IV) complexes with general formula PtL_2X_2 and PtL_2Cl_4, where L is thiacyclopentane- and thiacyclohexanespiro-5’-hydantoins and X^- is Cl^-were made. The IR, Raman, ^{1} H and ^{13}C NMR spectra were compared with the experimental data. There was very good correlation between experimental and theoretical results. Some physicochemical properties like molecular volume, dipole moment and logP were calculated. On the base of the analysis, the most probable bounding of the organic ligands with the metal ions in all the complexes was realized through the sulphur atom from the cycloalkane ring. The optimized geometric structures of the Pt(II) and Pt(IV) complexes with organic ligands were proposed.The complexes were tested for antitumor activity *in vitro* on panel of human tumor cell lines. The tested compounds exerted concentration-dependent cytotoxic effects against some of the tumor cell lines.

BS-Sy P06

Design and synthesis of new potential anticancer agent – 4-methoxy-salicylaldehyde isonicotinoylhydrazone

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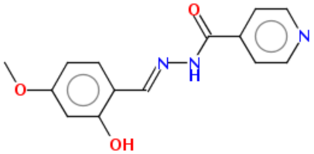
Salicylaldehyde benzoylhydrazone (SBH) is an unusually potent inhibitor of DNA synthesis and cell growth in a variety of cultured human and rodent cells. Aroylhydrazones derived from salicylaldehyde are compounds with interesting biological properties including a high anticancer activitiy.

The current study reports synthesis, DFT-calculations, physicochemical characterization and pharmacological investigations of a new derivative - 4-methoxy-salicylaldehyde isonicotinoylhydrazone (4mSIH). The hydrazone was prepared by the Schiff base condensation between isonicotinoyl hydrazide and 4-methoxy-salicylaldehyde in ethanol. The structure of the compound was confirmed by elemental and thermo-gravimetric analyses, IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

The cytotoxic effect of the new compound was examined on some human tumor cell lines using the MTT-dye reduction assay. The obtained IC_{50} values revealed that 4-methoxy-salicylaldehyde isonicotinoylhydrazone proved to be more active than cisplatin, and far more active than another utilized anticancer drug melphalan.



Acknowledgement: *The presented project has been financially supported by the Medical Science National Fund at the Medical University – Sofia (Project 63/2012)*

BS-Sy P07

Reactions of tetrahydro-isoquinolines *N*-ylides with non-symmetrical dipolarophiles

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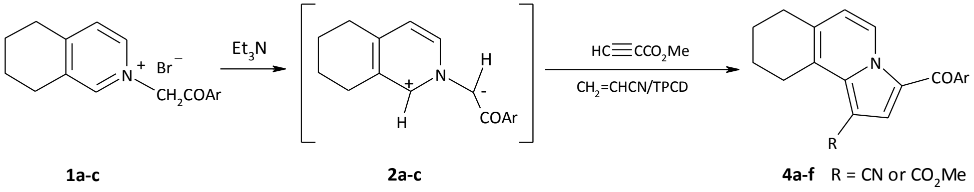
The versatile *N*-ylide 1,3-dipolar cycloadditions were successfully applied in generating various heteroatomic compounds with a high degree of complexity. [1]
The reaction between tetrahydro-isoquinolines *N*-ylides generated *in situ* from the corresponding bromides **1** and methyl propiolate as acetylenic dipolarophile gave directly 7,8,9,10-tetrahydro-pyrrolo[2,1-a]isoquinoline derivatives **4a-c.** Similarly, the cycloaddition reaction of tetrahydro-isoquinolinium *N*-ylides and acrylonitrile gave the 1,2,3,7,8,9,10,10a-octahydro-pyrrolo[2,1-a]isoquinoline. These were dehydrogenated in DMF with tetrakis-pyridinocobalt(II) dichromate (TPCD) as oxidant, at 90 °C, giving 7,8,9,10-tetrahydro-pyrrolo[2,1-a]isoquinoline derivatives **4d-f.** The bromides **1a-c** were prepared in yields over 90% from 5,6,7,8-tetrahydro-isoquinoline and the corresponding substituted 2-bromoacetophenones.



The structures of 7,8,9,10-tetrahydro-pyrrolo[2,1-a]isoquinolines **4a-f** were assigned by IR, NMR spectroscopy and confirmed by X-ray analysis.

References:

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BS-Sy P08

Interaction of Ru(II)-terpyridine complexes with some nitrogen- and sulfur-donor ligands

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More recently, a large interest has grown in ruthenium polypyridyl complexes as alternative drugs to cisplatin in cancer chemotherapy. In particular, the complex *mer*-$[Ru(tpy)Cl_3]$ and α-$[Ru(azpy)_2Cl_2]$ (azpy = 2-phenylazopyridine) showed significant in vitro cytotoxicity [1, 2]. Their mechanism of antitumor activity is believed to involve the formation of the Ru-DNA adduct by substitution of the chloro ligand with DNA. Recently, we developed a series of new polypyridyl complexes of the general formula [Ru(mtl)(chel)(X)][Y]*n* (mtl = 2,2',2''-terpyridine (tpy) or substituted tpy; chel = *N*-*N* or *N*-*O* chelating ligands; X = Cl or dmso-S; Y = Cl or PF_6; *n* depends on the nature of chel and X) as potential antitumor agents.

The goal of this work was to investigate the factors that influence the activity of our polypyridyl complexes and in particular how the nature of the chelating ligand influences the behavior of such complexes. Thus, we have used various N,N-chelating ligands, such as ethylendiamine or trans-1,2-diaminocyclohexane, while the sixth position was occupied by Cl. We have studied the reactions of two polypyridyl complexes, [Ru(tpy-Cl)(en)Cl]Cl and [Ru(tpy-Cl)(dach)Cl]Cl, with nitrogen- and sulfur- donor ligands such as pyrazole, 1,2,4-triazole, L-cysteine, L-methionine and thiourea. The characterization of the final products and intermediates was performed in solution using NMR spectroscopy. The thermodynamics and kinetics of selected reactions were studied using UV-Vis spectrophotometry.

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BS-Sy P09

Synthesis and structure of copper(II) complex with pyridoxal S-methylisothiosemicarbazone

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Metal complexes with Schiff bases of pyridoxal, as one of six natural forms of vitamin B6, are subject of different kinds of research, due to interesting chemical, structural and biological properties [1]. A special group of pyridoxal Schiff bases are semi-, thiosemi- and isothiosemicarbazones which were found to behave as tridentate ONO, ONS and ONN ligands, respectively [2]. A limited number of transition metal complexes with pyridoxal S-methylisiothiosemicarbazone (PLITSC) are known, in which this tridentate ONN ligand coordinates either in neutral, mono- or dianionic form, which was proved by structural analysis of several complexes [2–4].

Here we describe synthesis and crystal structure of the first Cu(II) complex with monoanionic form of PLITSC of the formula [Cu(PLITSC-H)H_2O]Br·H_2O. The complex is obtained by reaction of $CuBr_2$ and PLITSC in 1:1 mole ratio in warm 80% ethanol. Crystal structure analysis showed that copper atom is situated in a square-planar environment made by tridentate ONN coordination of ligand and one water molecule (Fig. 1.). Chelate ligand is coordinated through phenoxide oxygen, azomethine and isothioamide nitrogen atoms in monoanionic form, in which pyridoxal moiety retains zwitter-ionic form. Tridentate coordination of PLITSC results in formation of two planar metallocycles, one five membered (isothiosemicarbazide) and the other six membered (pyridoxilidene). The same coordination mode in monoanionic form was found in [VO_2(PLITSC–H)]·$2H_2O$ [4]. Besides ionic interaction, association of the complex molecules in the solid state is determined by the presence of multiple intermolecular hydrogen bonds.

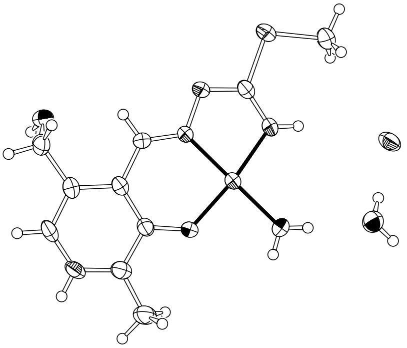

Fig. 1. Molecular structure of [Cu(PLITSC-H)H_2O]Br·H_2O

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BS-Sy P10

Synthesis of some new oximino-D-modified androstane derivatives

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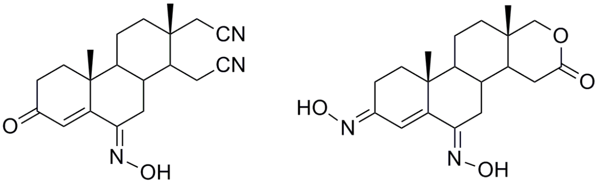
Steroidal oximes and their derivatives have interesting bioactivity and known to exhibit anti-inflamatory, anticancer and other types of physiological activity. These compounds represent a distinct class of antineoplastic agents and studies have revealed that the cytotoxicity of these compounds against cancer cells is dependent on the location of the oximino group on the steroidal nucleus. The parental steroids with an oximino group located at the 3- or 6-position show a remarkable difference in their cytotoxicities. Getting in consideration mentioned facts, in this report we present multistep synthesis of some new potential steroidal cytotoxic agents **1** and **2** (Figure 1.), with oximino function at C-6 and C-3 position, starting from dehydroepiandrosterone.



1 **2**

Figure 1.

Acknowledgement: *Authors would like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project ON172021)*

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BS-Sy P11

Microwave assisted reduction of individual naphthenic acids

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The aim of this paper is to modify the conventional method of reduction of carboxylic acids with metal hydrides. Under modifications, we perform the reaction in a microwave reactor, solvent-free and without conventional heating, and with significantly shortened duration of the reaction. We optimized the process of reduction by adapting working conditions in the microwave reactor. We studied the reduction of selected individual naphthenic acids: benzoic-, cyclohexylacetic-, 4-cyclohexylbutanoic- and cyclohexyl-carboxylic acid to corresponding alcohols by NaBH4 and in the presence of LiCl as a catalyst. The reductions were performed in a monomode CEM microwave reactor directly from the free acid in the absence of solvent. Reactions were performed at three molar ratios of substrate: NaBH4: LiCl (1:1:1, 1:2:2, 2:1:1) at 80 °C and time interval of 30 seconds to 30 minutes. The best results, 90-90 % yield, were obtained in the range of 30-60 s with acid ratio: NaBH4: LiCl (1:2:2). The reduction of carboxylic acids performed in a microwave reactor produces up to 1400 time shorter reaction duration than using conventional methods with heating.

BS-Sy P12

Microwave-assisted oxidation of bile acids by Oxone/$AlCl_3$ in water

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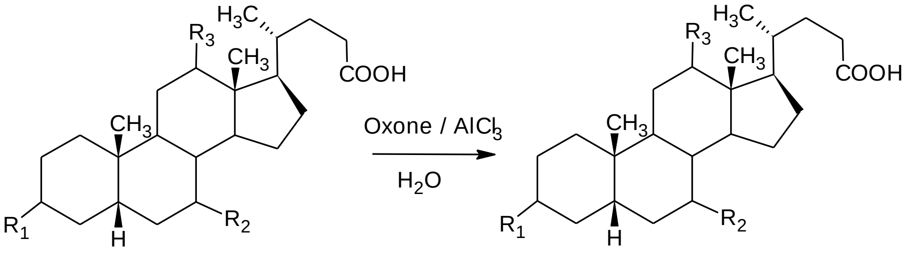
Oxidation of hydroxyl functional groups to their corresponding carbonyl compounds is one of the most important and challenging transformations in the synthesis of various compounds and intermediates. In contrast to traditional methods that require use of large amount of transition-metal involved noxious oxidants, non-green organic solvents or severe reaction conditions, we have found that in water media aluminum chloride plays a dominant role in the bile acid oxidation in the presence of Oxone.

In deionized water, at room temperature, the oxidation of 3α,12α-dihydroxy-5β-cholanoic acid (deoxycholic acid, DCA), as a model compound, with Oxone /$AlCl_3$ system afforded high yield of 3,12-dioxo-5β-cholanic acid after three hours. Reaction progress was monitored by TLC (solvent system $CHCl_3$/$(CH_3)_2CO$, 60:40, v/v). Further optimization of the reaction conditions in a Discover Bench Mate microwave reactor (CEM, maximum output power 300 W, Synergy software), gave 3,12-dioxo-5β-cholanic acid at 50 °C and 12 minutes of microwave irradiation (yield 81%). Similar results were obtained for chenodeohycholic (CDCA), cholic and lithocholic acid (CA and LCA). Compared to the conventional protocol, a remarkable reduction in the overall processing time from hours to a few minutes was achieved. Structures of the synthesized bile acids oxo-derivatives have been confirmed by ^1H- and ^{13}C- NMR spectroscopic data.



Bile acid	R_1	R_2	R_3
CA	α-OH	α-OH	α-OH
LCA	α-OH	H	H
DCA	α-OH	H	α-OH
HDCA	α-OH	α-OH	H

Product	R_1	R_2	R_3
Dehydro-CA	=O	=O	=O
Dehydro-LCA	=O	H	H
Dehydro-DCA	=O	H	H
Dehydro-CDCA	=O	=O	H

The obvious advantages of the present protocol of bile acids oxidations include green reaction media applying deionized water as sole solvent. This environmentally friendly method produced negligible quantities of hazardous waste, wide functional group tolerance, convenient product isolation, as well as multigrams reaction scale.

This work was supported by IPA Grant No: HUSRB/1002/214/193.

BS-Sy P13

Synthesis and antiproliferative activity of secoandrostane 17-mesilates

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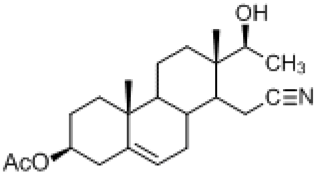
Prostate cancer continues to be one of the biggest health problems for the aging male. On the other hand, estrogen dependent breast cancer is the most commonly diagnosed cancer among women and continues to be a major cause of cancer deaths. In our previous work 3β-acetoxy-(17)-mesyloxy-17a-methyl-16,17-secoandrost-5-ene-16-nitrile (**3**)[1] was synthesised from corresponding 17-hydroxy derivative. In this study we used D-seco alcohol, for which we assumed to be a mixture of epimer alcohols **1** and **2**. This assumption was confirmed by isolation of stereoizomeric D-seco mesyloxy derivatives **3** (78 %) and **4** (9 %) after the mesylation reaction of mixture of compounds **1** and **2** with methanesulfonyl chloride (mesyl chloride) in absolute pyridine at 4 °C. Structures of compounds **3** and **4** were validated by IR, NMR and high-resolution mass spectroscopy (HRMS) spectra and by X-ray crystallography data. As a preliminary test for biological activity, products were screened for anti-proliferative activity *in vitro* against six human tumor cell lines and one human non-tumor cell line, while influence on the cell cycle and inducing of apoptosis was studied on population of MDA-MB-231 cell line.



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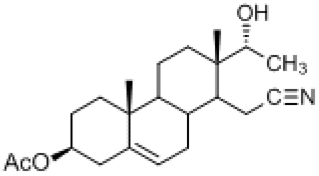

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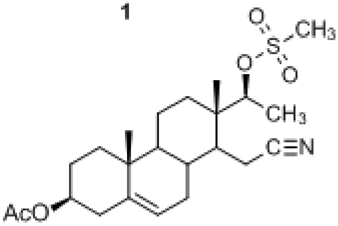

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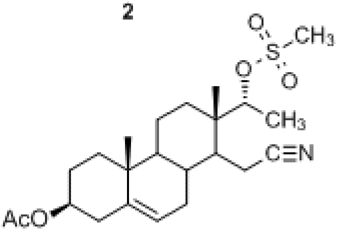

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Acknowledgement*: Authors would like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project ON172021)*

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BS-Sy P14

Evaluation of passive human skin permeability and human skin retention of newly synthesized 17β–carboxamide derivatives of methylprednisolone using PAMPA test

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The aim of this study was to evaluate passive human skin permeability and human skin retention of five newly synthesized 17β-carboxamide derivatives of methylprednisolone (MP) using PAMPA (*Paralel Artificial Memebrane Permeability Assay*) test. These derivatives are potential soft corticosteroids with local anti-inflammatory activity.
PAMPA test was carried out using hydrofobic PVDF 96-well plates. Each well was coated with the mixture of 70% silicone oil and 30 % isopropyl myristate (v/v) which simulates the *stratum corneum* of human skin [1,2]. The compounds were tested at iso-pH conditions (pH=5.5) in triplicates. Tested compounds in donor, acceptor plates and in starting solutions were determined using LC-MS tecnique monitoring corresponding parent ions (m/z) under negative HESI mode. The structures of tested compounds as well as calculated parameters $C_A(t)/C_D(0)$ (representing permeability) and R (representing retention in the artificial membrane) are presented in Figure 1. Single factor ANOVA was used to test the obtained results.

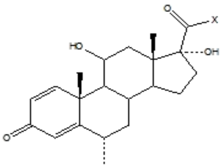
Compound	X		$C_A(t)/C_D(0)$%	R %
MP	$-CH_2OH$		1.35±0.06	0.94±0.17
MPG	$-NHCH_2COOCH_3$		0.55±0.05	1.23±0.31
MPA	$-NH(CH)CH_3COOCH_3$		1.37±0.06	1.67±0.12
MPEG	$-NHCH_2COOCH_2CH_3$		0.94±0.16	2.32±1.81
MPEA	$-NHCH_2CH_2COOCH_2CH_3$		1.37±0.10	6.47±1.40
MPF	$-NH(CH)C_6H_5COOCH_3$		11.56±0.19	7.89±1.29

Figure 1: Structures, $C_A(t)/C_D(0)$ and R of tested compounds

In comparison with methylprednisolone, derivative MPEA has similar permeability and significantly higher retention in the artificial membrane. These properties can positively contribute to its potential local anti-inflammatory activity with minimal systemic side effects when applied topically on skin.

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BS-Sy P15

Synthesis of Warfarin derivatives (Aa A Blood Anticoagulant) Catalyzed under Preyssler Heteropolyacids

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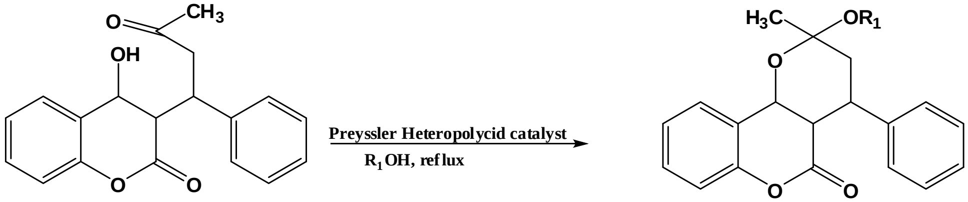
Coumarin and its derivatives form an elite class of compounds; they represent the ring systems of several important groups of natural products. They have been used as anticoagulants [1]. In continuation of our investigations in the field of the synthesis of coumarin derivatives, the synthesis of heterocyclic condensed 4-hydroxycoumarin derivatives is described herein. In the previous syntheses of a warfarin cyclic acetal, as a blood anticoagulant [2], Lewis acids were used as catalysts (zinc chloride, iron (III) chloride). In this reaserch, we report the synthesis of warfarin acetals by using Preyssler's anion and heteropolyacids (HPAs) catalysts, $H_{14}[NaP_5W_{30}O_{110}]$. By this conditions, we have excellent yields, and high selectivity. Preyssler heteropolyacid catalyst were easily recycled, recovery and reused without loss of its catalytic activities.



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BS-Sy P16

Solvent and substituent effects on azo-hydrazone tautomerism of some arylazo pyridone dyes

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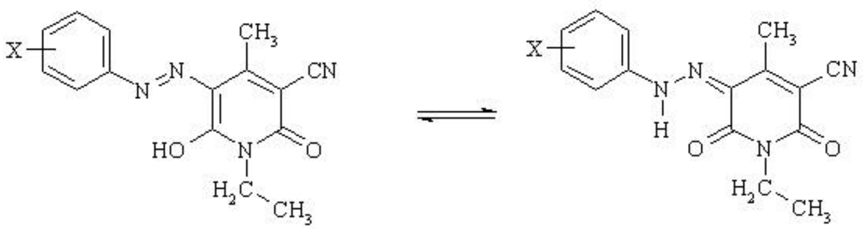
Disperse monoazo dyes having pyridones as the coupling component exhibit azo-hydrazone tautomerism [1,2]. In this work, ten dyes having the same 1-ethyl-4-methyl-6-hydroxy-3-cyano-2-pyridone have been synthesized (Fig. 1) and fully characterized by melting point, FTIR, ^{1}H and ^{13}C NMR spectroscopy. Solvatochromism and tautomerism of these dyes have been investigated in twenty one solvents of different polarity. The effects of specific and non-specific solvent/solute interactions on the position of their UV/Vis absorption bands have been evaluated using the Kamlet–Taft and Catalán solvent parameter sets. Furthermore, the effects on the solvatochromic behaviour of different substitution patterns on the aryl moiety have been examined.



X: 1) *o*- OCH_3 , 2) *m*- OCH_3, 3)*p*- OCH_3 ,4) *o*- NO_2 , 5) *m*- NO_2,
6) *p*- NO_2 , 7) *o*-Cl, 8) *m*- Cl, 9)*p*- Cl 10) H

Figure 1. Azo-hydrazone tautomerism of investigated arylazo pyridone dyes

Acknowledgements: *The authors acknowledge the financial support of the Ministry of Education and Science of Republic of Serbia (Project 172013)*

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BS-Sy P17

Preparation and spectral characterization of Pt(II) and Pt(IV) dithiocarbamato complexes

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Platinum complexes are known therapeutic agents in medicine[1]. Cisplatin in particular is one of the very well known drugs for treatment of various cancers[2]. It is also documented that the negative side-effects of these drugs can be greatly reduced by the use of sulfur-containing compounds. Dithiocarbamates were evaluated as potential protectors of the kidneys from cisplatin[3]. Thus, the importance of studying dithiocarbamato platinum complexes increases.

Here, the preparation and spectral characterization of the platinum (II) and platinum (IV) complexes with dithiocarbamato ligand (idadtc^{3-}), based on iminodiacetate, is reported. In the reaction of K_2PtCl_4 and K_2PtCl_6 salts with ammonium salt of idadtc^{3-} and HCl in stoichiometric ratio 1:2:4, and 1:3:6, the corresponding Pt(II) $(H_2idadtc)_2$ and Pt(IV) $(H_2idadtc)_3$ complexes were isolated as yellow and brownish solids, respectively.

The complexes were characterized by elemental analysis, IR and UV-Vis spectroscopy. The results confirm the coordination of the dithiocarbamato ligand to Pt(II) and Pt(IV) ions through the sulfur atoms of dithiocarboxy group. -NCSS moiety acts in both cases as a symmetrical bidentate chelating group. Square-planar geometry of the coordination sphere is proposed for the Pt(II) complex, and the octahedral geometry for the Pt(IV) complex.

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BS-Sy P18

Synthesis and structure of copper(II) complex with pyridoxalaminoguanidine and 4-picoline

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Considering certain adverse pharmacological activity of aminoguanidine (AG), as one of the most powerful inhibitors of carbonyl stress and the occurrence of diabetic complication, the examination of its Schiff bases with aromatic compounds was initiated. These Schiff bases seem to have the same efficiency as AG itself, but are far more safe to use [1]. Among them, the Schiff base with pyridoxal (PL), one of the forms of vitamin B6, occupies a special place [2,3]. Namely, the active form of vitamin B6, pyridoxal 5'-phosphate (PLP), has a significant role in various metabolic, biosynthetic and regulatory processes [4]. Thus, it seems worthwhile to examine the properties of transition metal complexes with pyridoxalaminoguanidine (PLAG).

Here we present the synthesis and structure of copper(II) complex with PLAG and 4-picoline, of the formula [Cu(PLAG–H)(4-pic)MeOH]NO_3. Single crystals of the complex were obtained by the reacton of warm methanolic solutions of $Cu(NO_3)_2$ and PLAG in the presence of the excess of 4-picoline. The complex was characterized by elemental analysis, conductometric measurements, IR spectra and X-ray analysis. Cu(II) is coordinated by two oxygen and three nitrogen atoms to form an almost ideal (τ = 0.056) square-pyramidal environment: O1, N1 and N3 from the monoanion of the chelate ligand and N6 of 4-picoline in the basal plane and O3 of the methanol molecule in the apical position (Fig.1.). PLAG is coordinated as a monoanion, formed by the deprotonation of the previously described zwitter-ionic form, i.e. nitrogen atom of the PL residue. Cu(II) is shifted from the equatorial plane toward the apical O3 ligator for 0.116 Å. Pyridine ring of the PL moiety, 5-membered metallocycle and pyridine ring of 4-picoline are planar, whilst 6-membered chelate ring has a conformation close to 'screw-boat'. Crystal structure of the complex is stabilized by the extended network of intermolecular H-bonds.

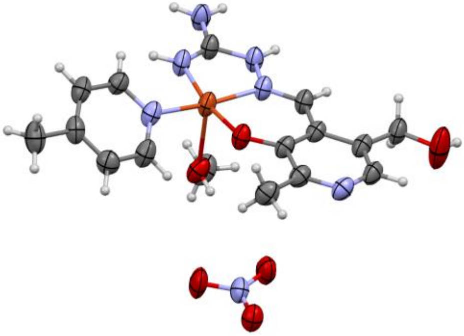
Fig. 1. Molecular structure of [Cu(PLAG–H)(4-pic)MeOH]NO_3

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BS-Sy P19

Antioxidant, antiproliferative and enzyme inhibition activity of new salicyloyloxy androstane derivatives

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Important roles in cancer formation, among other factors, play damaging effects of free radicals. Knowing that salicylic acid, being phenolic compound, express scavenger potency, we postulated that steroidal salicylic acid derivatives could express scavenger potency also. Thus a series of salicylic acid derivatives of androstane was synthesized, applying conventional heating and/or microwave irradiation methods, with salicyloyl function in position 3 or 17 or in both positions. Reaction times and yields of conventional and microwave-assisted syntheses were compared. Structures of all new compounds were characterized based on NMR, IR and mass spectra, while the X-ray crystal structures of some compounds were determined. Almost all new compounds expressed scavenger potency, while several compounds expressed antiproliferative activity against tumor cells, with no cytotoxic effect on the healthy cells. Some compounds inhibited steroidogenic enzyme 17beta-HSD type 2.

Acknowledgement: *Authors would like to thank the Hungary-Serbia IPA Cross-border Co-operation Programme (Project No. HUSRB/1002/214/133 RECODAC) and to the Provincial Secretariat for Science and Technological Development of the Autonomous Province of Vojvodina (Grant No. 114-451-2713/2012-01).*

BS-Sy P20

Solvent-free amidation of naphthenic acids under microwave irradiation

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The stable and polar amide functionality is an important unit among the organic molecules present in natural-occurring materials, peptides and proteins. It is also found in many synthetic substances as intermediates or as active pharmaceutical products or prodrugs. Due to its interest several methods were developed for the synthesis of carboxamides, like conversion of carboxylic acid to a more reactive functional group or an in situ activation by using expensive coupling reagents. Although, good results are obtained with both approaches, long reaction time, use of organic solvents, hazardous reagents and by-products generation requiring further separations presents main drawbacks.

Within the framework of ‘Green Chemistry’, noticeable results were obtained utilizing solvent-free techniques and microwave activation in synthesis of amides under closed-vessel conditions and temperatures high above their boiling point. Starting from the equimolecular mixture (atom-economical synthesis) some of the least reactive secondary amine and carboxylic acid lead to the high yield (90 %) and purity of synthesized amide in 10 minutes of microwave irradiation. Efficient, uncatalysed amidations under solvent-free microwave irradiation were also confirmed on complex mixture of natural naphthenic acids as "Velebit" and comercial Aldrich naphthenic acids. Compared to the conventional protocol a dramatic reduction in overall processing time from hours to a few minutes was achieved.

Environmentally benign and efficient reactions of amidations were performed in Discover Bench Mate microwave reactor (CEM, maximum output power 300 W, Synergy software) in closed-vessel system. Structures of synthesized amides have been confirmed by 1H NMR- and 13C NMR-spectroscopic data.

BS-Sy P21

Reactivity of some oxo bile acids oxazolines in Wittig reaction

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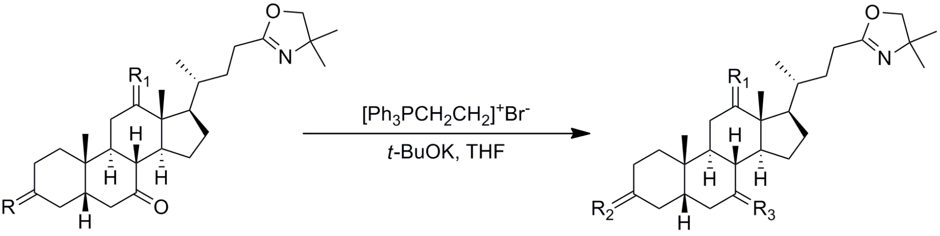
Bile acid salts are amphiphilic steroid molecules which, depending on hydrophobicity of β side of steroid nucleus, forming micelles able to bind hydrophobic drugs. However, above critical micellar concentrations bile acid salts damage cell membrane. Oxo derivatives of bile acid have decreased membranotoxicity but also their solubilisation capacity is lowered. The aim of our project is the synthesis of some derivatives with bigger hydrophobic area of lateral sides of molecule without introducing new carbon atoms on β side of steroidal skeleton.

There are only few published Wittig reactions of steroidal skeleton, especially of bile acids, and the olefination was successful only at C3 carbonyl group.[1,2] We have explored reactivity of different oxo bile acids oxazoline derivatives under Wittig reaction conditions (Scheme 1). We have found that the mono-oxo derivative **1** stereoselectively gives 7(*E*)-ethylidene product **4**, while dioxo compound **2** in same reaction conditions yields regio and stereoselectively product **5**. Wittig olefination of molecule **3**, containing three oxo groups, gives equimolar mixtures *E* and Z of 3-monoethylidene products **6**, and of 3(*EZ*), 7(*E*)-diethylidene isomers **7**.



1 R, R_1= αOH, βH
2 R= αOH, βH ; R_1= O
3 R, R_1= O

4 R_1,R_2= αOH, βH; R_3= *E* $CHCH_3$
5 R_1= O; R_2= αOH, βH; R_3= *E* $CHCH_3$
6a,b R_1= O; R_2= (*EZ*) $CHCH_3$; R_3= O
7a,b R_1= O; R_2= (*EZ*) $CHCH_3$; R_3= (*E*) $CHCH_3$

Scheme 1.

***Acknowledgement**: The work was supported by a grant from the Ministry of Education and Science of Republic of Serbia (Project no. 172021).*

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BS-Sy P22

Synthesis and anti-proliferative activity of new heterocyclic androstane compounds

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Endogenous androgens play a role in the development and progression of prostate cancer and estrogens plays a crucial role in the development of breast cancer. Some steroidal compounds with heterocyclic groups are potent inhibitors of steroidogenic enzymes and potential anti-cancer agents which inhibit proliferation of cancer cells. Building on our previous work on D-homo fused steroidal tetrazoles[1] and 17-picolyl and 17-picolinylidene androstane derivatives[2] we synthesized new compounds **1**- **4** (Figure 1). Compounds were evaluated as potential anti-proliferative agents against a panel of human cancer cell lines and one human non-tumor cell line, MRC-5.

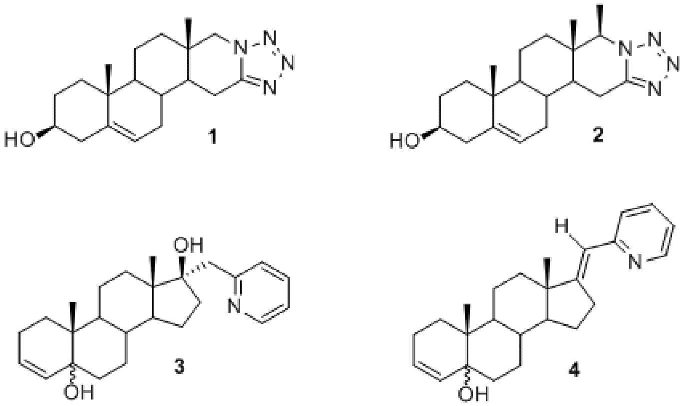

Figure 1. Structures of newly synthesised compounds

Acknowledgement. *Authors would like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project ON172021)*

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[1] K. M. Penov- Gaši, A. M. Oklješa, E. T. Petri, A. S. Ćelić, E. A. Djurendić, O. R. Klisurić, J. J. Csanadi, G. Batta, A. R. Nikolić, D. S. Jakimov, M. N. Sakač, *Med. Chem. Commun.* **4** (2013) 317

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BS-Sy P23

Synthesis of Diazepines (As Therapeutic compounds) by Green Heteropolyacids Catalysts

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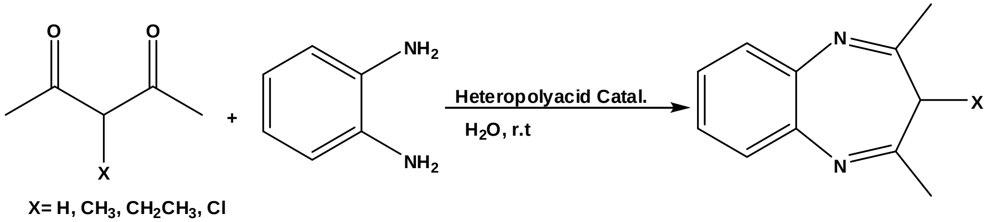
Benzodiazepine derivatives also find commercial use as anti-inflammatory agents [1]. Benzodiazepines have recently received great importance because of their wide range of therapeutic and pharmacological properties. Many members of diazepine family are nowadays widely used as anticonvulsant, antianxiety, analgesic, sedative, antidepressive, and hypnotic agents [2]. In this work, we investigated the synthesis of benzodiazepines using Preyssler type heteropolyacid, $H_{14}[NaP_5W_{30}O_{110}]$ and Wells-Dawson, $H_6P_2W_{18}O_{62}$ and $H_4PMo_{11}VO_{40}$. We extended to the synthesis of various diazepines by the condensation of diamines with various 1,3-diketones in aqueous state.



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BS-Sy P24

Oxidative decarboxylation of some benzyilic acids by Cu(III) complexes

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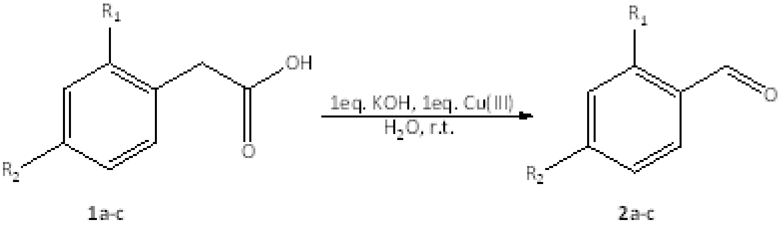
Oxidation with copper(III)

Periodate complexes of copper in its trivalent state have been extensively used in the analysis of some organic compounds [1-2]. Copper complexes have occupied a major place in oxidation chemistry due to their abundance and relevance in biological chemistry [3–4].
The highly efficient oxidative decarboxylation of different phenylacetic acids with Cu(III) complexes is described. In the presence of this complexes phenylacetic acids (1a-c) were converted to their corresponding aldehyde compounds (2a-c) via oxidative decarboxylation reaction (Scheme 1).



Scheme 1

As shown in Table 1, the reaction of the different phenylacetic acids 1a-c leads to the formation of the corresponding aldehyde compounds 2a-c in good yields. Spectroscopic data were obtained for all products which were characterized by ^{1}H, ^{13}C NMR and IR spectroscopy.

Product	R_1	R_2	Yields (%)
2a	H	H	86
2b	H	Cl	92
2c	$C_6H_3Cl_2NH$	H	98

Table 1. *Yields of aldehyde compounds (2a-c) obtained by Cu(III) oxidative decarboxilation*

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BS-Sy P25

Miniemulsion polymerization of styrene in the presence of different layered silicates

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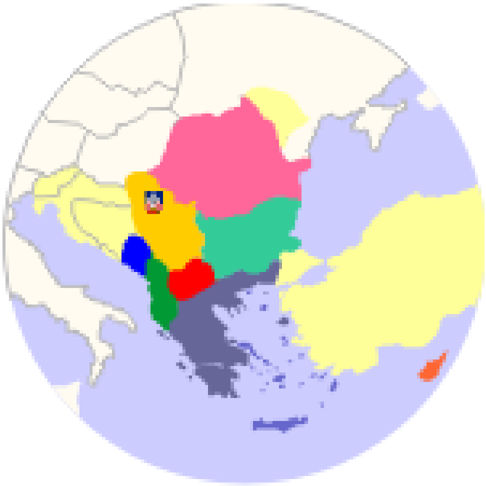
Polymer-clay nanocomposites were intensively studied over the past decade because of their enhanced properties compared with traditional composites. In present work, the possibility to obtain stable nanocomposite latexes based on styrene with/without layered silicate using miniemulsion polymerization procedure was followed. The final products were characterized by DLS, FTIR, TGA, DSC and ESEM. The presence of the clays influences the average diameter of the particles and the size distribution, as it was shown by DLS analyses. FTIR spectra of the nanocomposites proved the existence of the specific peaks of the clays. X-Ray diffraction patterns suggested mostly an intercalated structure of polymer-clay nanocomposites. TGA and DSC data's showed an increased thermal stability in the presence of clay layers. The morphology of the final latex observed by ESEM, revealed the presence of polymer-clay aggregates.

Acknowledgment: *This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI– UEFISCDI, project number 3.2-1391.*



Analytical Science

O 04 BS-AS

Kinetic analysis of thermal degradation of binuclear hexaaqua-μ_2-pyromellitato-bis(ethylenediamine)dinickel(II) tetrahydrate

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Most studies concerning ternary transition metal complexes with tetraanion of pyromellitic acid, pyr^{4-}, and diamine ligands are focused on structural properties [1], while thermal behavior of such complexes is much less investigated. The synthesis and crystal structure of the title complex, $[Ni_2(en)_2(pyr)(H_2O)_6]\cdot 4H_2O$, where en is ethylenediamine, have been published elsewhere [2]. Here, we report the kinetic analysis of thermal degradation of the complex investigated by TG/DSC analysis under non-isothermal conditions. TG/DCS data were collected at four different heating rates: 5, 10, 15 and 20 ºC min^{-1}.

The decomposition of the complex starts with dehydration process, which is well separated step in TG curve and occurs between room temperature and 199 ºC. The anhydrous complex further decomposes in two partially overlapped steps. The first one in the temperature range 199 – 349 ºC can be related to decarboxylation (loss of CO) and escape of 2 mole of en. The removal of remaining organic fragments could be assumed in the final step up to 464 ºC. Intermediate products obtained after heating at 213 and 350 ºC were characterized by FT-IR spectroscopy, while the residue was analyzed by XRD in order to obtain more profound insight.

Degradation enthalpies, thermodynamic activation parameters, pre-exponential factor, A, and the apparent activation energy, E_a, were determined for each step using Kissinger's and Ozawa's equations. The dependence of E_a on conversion degree, α, calculated by means of Kissinger-Akahira-Sunose, Starink and Li-Tang isoconversional methods [2], showed that all three steps are complex involving more than one elementary step. In order to find these elementary steps, processes I and II were deconvoluted using a cross product of Gaussian and Lorentzian function. Step I was divided into two, whereas step II was separated into three elementary steps. The obtained single-step processes were further analyzed and discussed in the term of proposed mechanism for thermal decomposition of the complex.

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O 05 BS-AS

LC-MS analysis of pharmaceutical and pesticide residues in wastewater and surface water

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In the recent years, pharmaceuticals and pesticides have been frequently detected in aquatic ecosystems. Since significant amounts of pharmaceuticals and pesticides present in the aquatic environment originate from the urban wastewater, the control of such compounds has become an important topic of water monitoring and analysis. Seven pharmaceuticals and fourteen pesticides were selected for this study. Methods separately developed for analysis of pharmaceutical and pesticide residues in surface and ground water were combined in a single multiresidual method that was applied to the wastewater samples after validation [1,2]. The technique is based on solid-phase extraction combined with liquid chromatography coupled with tandem mass spectrometry using positive electrospray ionization. The sample preparation consisted of solid-phase extraction of 100 mL of the sample (pH = 6) on Oasis HLB cartridge, and elution with methanol-dichloromethane (1:1) mixture. Method detection and quantification limits were in the range of 0.21 to 5.5 ng L^{-1} and 0.7 to 18.2 ng L^{-1}, respectively for all analysed compounds, with recoveries from 72 to 129% in surface, as well as wastewater samples. All results displayed a good degree of reproducibility, with the relative standard deviations (RSD) less than 20%. Wastewater samples were collected at three different sampling sites of the municipal wastewater discharges in Belgrade. The surface water samples were taken downstream from the wastewater discharge, in the middle of the river, where wastewater has been mixed with the recipient. In wastewater samples the most frequently found analytes were pesticide carbendazim, and pharmaceuticals lorazepam and diclofenac, while in surface water samples the most frequently found were pesticide carbendazim, and pharmaceutical trimethoprim.

Acknowledgements: *The authors thank the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172007) for providing financial support.*

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BS-AS P01

Thermodynamic study of binary mixture dimethyl adipate + PEG400 at T = (288.15 – 323.15) K

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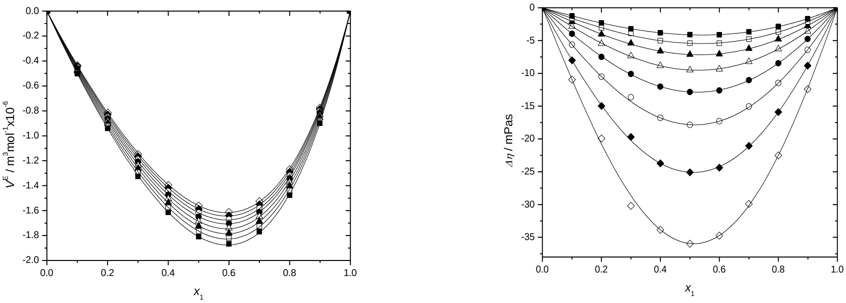
Dimethyl adipate (DMA) is a non-volatile, low toxicity, readily biodegradable specialty organic solvent [1]. It is used as a chemical intermediate (polymers, agrochemicals), a specialty solvent (inks, coatings, adhesives), an emollient and can also be utilized as a paint remover and plasticiser. Polyethylene glycol (PEG) is a nontoxic, highly biodegradable polymer [2]. It is also well known as a food-additive [3,4] and is used for various biological and bio-medical applications in aqueous solutions with biological macromolecules [5]. In this work experimental density, viscosity and refractive index of binary mixture dimethyl adipate + PEG400 were measured at eight temperatures (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15, 323.15) K and at atmospheric pressure. Excess molar volume V^E, deviations of viscosity $\Delta\eta$, and refractive index Δn_D were correlated using Redlich-Kister equation. V^E and $\Delta\eta$ values (Figure 1) are negative over the entire composition range, while Δn_D values exhibit positive trend.



a) b)

Figure 1 - Experimental values of: a) V^E and b) $\Delta\eta$, for the system DMA (1) + PEG400 (2) at the following temperatures: (◊) 288.15 K, (♦) 293.15 K, (○) 298.15 K, (●) 303.15 K, (Δ) 308.15 K, (▲) 313.15 K, (□) 318.15 K, (■) 323.15 K, (——) RK equation.

The authors gratefully acknowledge the financial support received from the Research Fund of Ministry of Education and Science (project No 172063).

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BS-AS P02

Extraction optimization of sterols and hormones from river sediments

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Sterols and hormones are regarded as emerging contaminants of environmental concern [1]. As a consequence of their incomplete removal from urban effluents, they can be found in environmental samples, *i.e.* natural waters and sediments. As a result of accumulation, high concentrations of these analytes are particularly present in river sediments [2]. This study describes development and optimization of the method for extraction of twenty selected human, animal and plant sterols, and hormones from sediments at ng g^{-1} levels. In the method development, extraction solvent and weight of the sediment for extraction were optimized, with the aim of achieving higher preconcentration factor and extracting lower amount of impurities. For reducing analysis time, extraction time in the ultrasonic bath was also optimized. The recoveries of the optimized method were high (80.7–120.4 %) with the relative standard deviations generally lower than 22 %. Sediment sample from the Morava River was extracted using the optimized method. The obtained extract was purified and analyzed by liquid chromatography–tandem mass spectrometry (LC–MS/MS) with atmospheric pressure chemical ionization (APCI). It was determined that human and animal sterols (epicoprostanol, α-cholestanol, β-cholestanol, cholesterol) in the range 0.76–2.94 µg g^{-1}, as well as plant sterols (stigmastanol, stigmasterol, campesterol, β-sitosterol) in the range 0.52–2.21 µg g^{-1}, were present in the river sediment (Fig. 1).

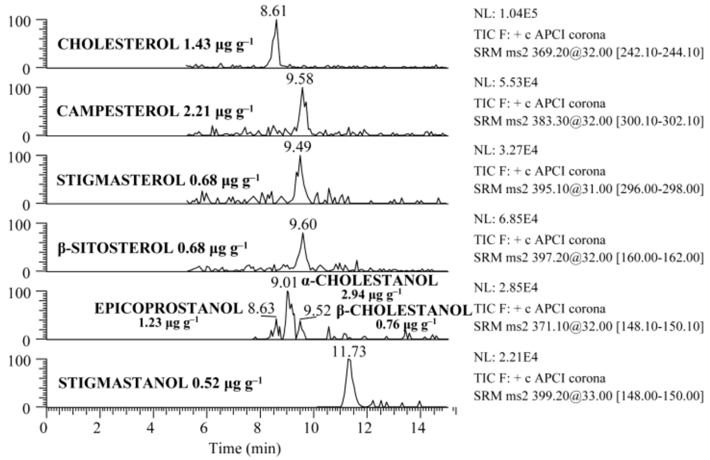

Fig. 1. Chromatogram of the sediment sample from the Morava River with amounts of detected sterols

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BS-AS P03

Analysis of snow chemical composition based on IC method

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In last years, ion chromatography (IC) become the recommended method for air quality, proved to be a simple, fast, small volume sample demanding and reliable method for determination of anions and cations in aqueous samples.

The chemical composition of wet depositions was carried out from December 2012 to March 2013 in Bucharest, Romania [1]. Ten sampling sites were selected and 50 snow samples were collected in this period. The results of this study were compared to the earlier published data [2].

All samples were analyzed for pH, major anions (F^-, Cl^-, NO^{3-} and SO_4^{2-}) and major cations (K^+, Na^+, NH_4^+, Ca^{2+} and Mg^{2+}. The equipment used is an automated ion chromatograph ICS3000 Dionex gifted with conductivity detector for ion analysis. Most of the wet deposition samples prezented alkaline pH (pH > 5.6).

Measurements gived values within the 1.2 –21.7, 0.59 – 1.05, and 0.58–1.08 mg/L for Cl^-, NO^{3-} and SO_4^{2-} respectivel and 3.11 – 32.75, 0.47 – 12.39, 51.9 – 157.16, 4.29 – 27.4 and 23.81 – 162.5 mg/L K^+ , Na^+, Ca^{2+} , Mg^{2+} and NH_4^+ respectively and a realistic indicative of atmospheric pollution for many urban areas.

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BS-AS P04

Uptake of cadmium, copper, iron, manganese, and zinc in some wild edible mushrooms from Serbian forest

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The consumption of wild growing mushrooms has been increasing in many countries. Especially in Eastern and central Europe mushrooms have high commercial value. In this study, 40 samples of Parasol Mushroom (Macrolepiota procera) [1-3] were collected in the vicinity of Krusevac and Trstenik, Serbia in autumn during 2011 year. Metal concentrations in caps and stipes of fruiting bodies were determined by inductively coupled plasma-mass spectroscopy (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-OES). Translocation factor was calculated for stalk and cups. Translocation is the process leading to the redistribution of a chemical substance, once it has been deposited on the parts of a plant, to the other parts that have not been contaminated directly. Translocation is important in predicting the contamination of edible parts of those plants that are not consumed whole.The mushroom samples were prepared for analysis using microwave acid digestion procedure (7 ml HNO_3 and 1 ml H_2O_2). The following elements were analized: Cd, Cu, Mn, Fe, and Zn. The analytical accuracy of the method was evaluated by using the Standard Reference Materials (TORT-2, lobster hepatopancreas reference material for trace metals). The distribution of metals in samples was investigated and discussed. Correlation analysis and two multivariate analysis methods (principal component analysis and cluster analysis) were carried out in order to provide better understanding of the nature of associations of trace elements in mushrooms.

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BS-AS P05

Active moss biomonitoring of lead isotopic composition in Belgrade urban area

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Mosses have proved to be suitable biomonitors for a wide range of atmospheric contaminants such as heavy metals [1], especially lead, since the Pb concentration measured in naturally growing terrestrial moss is closely related to the bulk atmospheric deposition [2]. Active moss biomonitoring using ‘‘bag technique’’ has shown to be very suitable for assessment of atmospheric pollution with emphasis on trace elements in urban area [3,4]. In this study active moss biomonitoring survey of lead isotopic composition in Belgrade urban area was performed. Samples of the moss *Sphagnum girgensohnii*, previously collected at the end of May 2011 from a pristine wetland area was packed in nylon net bags. The experiment was carried out in five street canyons situated in heavy traffic area. Moss bags were hung at heights of about 4 and 8 m for 10 weeks during the summer of 2011. Microwave digestion of the moss samples was performed with HNO_3 and H_2O_2. The lead isotopes were measured by inductively coupled plasma mass spectrometry. The range of $^{206}Pb/^{207}Pb$ isotopic ratio was 1.167-1.184 for samples at 4 m height, and 1.164-1.184 at 8 m height; $^{208}Pb/^{207}Pb$ isotope ratio for 4 and 8 m height was in the range 2.450-2.477 and 2.433-2.471, respectively. The results for moss bags exposed at both heights indicated that Pb is still presents in the environment although leaded gasoline was banned in Serbia at the beginning of 2011. Further measurements for other moss exposure heights and source identification analyses are in progress. Also, there is an intention to compare moss Pb isotope composition with another type of biomonitor – leaves of linden and chestnut studied in previous survey [5].

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BS-AS P06

The substituent influence on the FTIR and UV spectral data of 6-substituted nicotinic acids

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The FTIR and UV spectra of a series of 6-substituted nicotinic acids were determined and the effect of compound structure and the applied solvents was studied. In order to analyze substituent influence, the absorption frequencies corresponding to the carbonyl group of the examined compounds were correlated with Hammett equation $\nu = \rho\sigma + h$, where σ the matching substituent constants for the absorption band of a carbonyl group of the specific compound, and ρ represents the sensitivity of the examined band to substituent effect. Furthermore, UV spectra were recorded in different solvent and again the absorption frequencies corresponding to the carbonyl group were analyzed, this time by Kamlet-Taft equation, in order to quantitatively present solvent influence. The Kamlet-Taft equation is given in the form $\nu_{max} = \nu_0 + s\pi^* + a\alpha + b\beta$ where ν_{max} is the absorption frequency, π^* is a measure of the solvent polarity, α represents the scale of solvent hydrogen bond donor acidities and β represents the scale of solvent hydrogen bond acceptor basicities.

BS-AS P07

Quantitative Structure–(NP TLC) Retention Relationship Analysis of 1,2-O-Isopropylidene Derivatives of Aldohexoses

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The main purpose of the present study was identifying the most relevant *in silico* molecular descriptors that influence retention behaviour of the selected 1,2-O-isopropylidene derivatives of aldohexoses in normal-phase thin-layer chromatography on silica gel and applied cyclohexane-dioxane (70 : 30 v/v) solvent system [1]. These derivatives have conveniently been used as starting compounds and key intermediates in the synthesis of several biologically active molecules [2]. As a result of the experimental, computational and statistical analyses, multiple linear regression (MLR) model that relate chromatographic constant R_M^0 (dependent variable) with critical pressure (CP) and critical temperature (CT) (independent variables), was constructed. The statistical significance of the estimated MLR model was confirmed by standard statistical measures and *cross-validation* parameters ($s = 0.0816$, $F = 4$[illegible]27, $r = 0.9791$, $r^2_{CV} = 0.8266$, $r^2_{adj} = 0.9379$, $PRESS = 0.1116$) [3]. These parameters indicate the possibility of application of the established MLR model in prediction of the retention behaviour of studied derivatives and structurally similar compounds.

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BS-AS P08

Spectrophotometric investigations of substituents effects on azo- hydrazone tautomerism and p*K*a values of arilazo pyridone dyes

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Eleven arylazo pyridone dyes, 5-(4-substituted arylazo)-6-hydroxy-4-methyl-3-cyano-2-pyridone were synthesized [1] and their absorption spectra were recorded in water. The influence of substituents group in the diazo component of dyes on their absorption spectra was investigated. Azo-hydrazone tautomeric equilibrium and pKa values of synthesized dyes were determined by semiquantitative approach, based on the analysis of UV/Vis overlapping bands [2]. The results showed that absorption spectra and pKa values of dyes are notably dependent on substituent electronic effects, being quantified by Hammet equation (Fig 1).

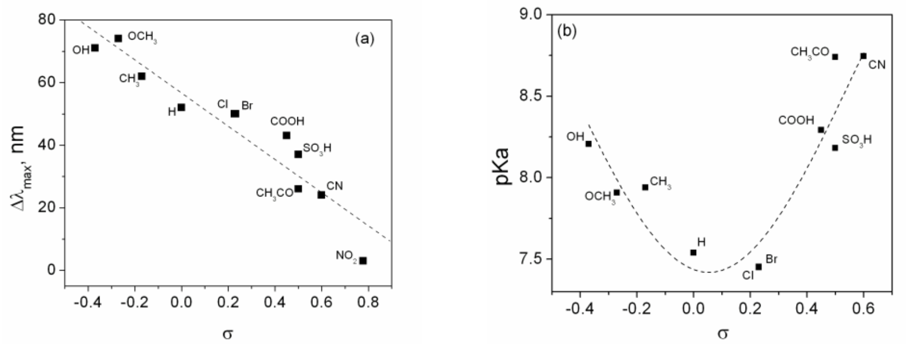

Fig. 1 (a) Relation between Δλmax ($\lambda_{hydrazo}$ - λ_{azo}) and Hammett constant, σ
(b) Relation between pKa values of dyes and Hammett constant, σ

This work was supported by the Ministry of Education and Science of the Republic of Serbia (Projects No. III45001).

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BS-AS P09

Pyrite as a sensor for potentiometric argentometric titrations in non-aqueous media and its use for pharmaceuticals' determinations

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Silver electrode, the most frequently used indicator electrode for argentometric titrations in water, suffers from adsorption of halide anions onto silver surface [1], which significantly influence on the electrochemical reactivity of the metal electrode. In this adsorption phenomena, non-aqueous solvents have also important role. For this reason, metal silver electrode is not convenient as an indicator electrode for determination of halides by potentiometric precipitation titrations in non-aqueous media. Taking this into account, pyrite as an indicator electrode for potentiometric argentometric determination in non-aqueous media has been investigated. The preparation of the pyrite electrode has been described earlier [2].

Pyrite electrode exhibits stable potential values against the time. Dynamic response time has been determinated in the sequence of low-to-high concentrations, as a ten-fold difference between silver ions ones (1.0 x 10^{-5} M to 1.0 x 10^{-1} M). Steady potential is achieved in a very short time, less than 20 seconds. Electrode produces a straight line over a wide concentration range (from 1.0 x 10^{-4} M to 1.0 x 10^{-1} M), with Nernstian slope of 63.6 mV and 59.3 mV per decade of concentration of silver ions in acetonitrile and propionitrile, respectively.

Due to pharmaceutical properties of verapamil hydrochloride (Figure 1), we consider that it is of interest to investigate whether it could be determinated by using pyrite electrode.

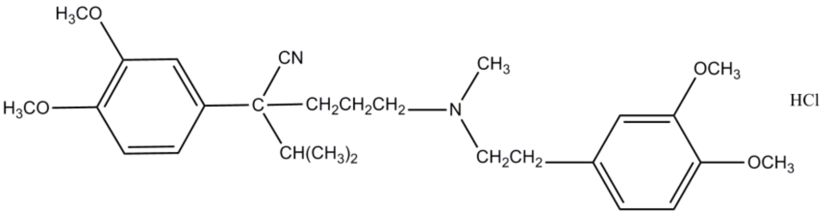

Figure 1.

Further, pyrite electrode has been applied as an indicator electrode in potentiometric titrations of hydroxylammonium chloride, choline chloride, tetrabutylammonium bromide, cetyltrimethylammonium bromide, potassium iodide, and ammonium thiocyanate with non-aqueous standard solution of silver nitrate, 0.1000 M, in acetonitrile and propionictrile. The standard deviation of the determination of the investigated substances was 0.21 %-0.49 %.

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BS-AS P10

A quantitative structure-retention relationship study of 1,2,4,5-mixed tetraoxanes

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The chromatographic behavior of 1,2,4,5-mixed tetraoxanes, cholic and deoxycholic acid derivatives with observed biological activity, was examined by high-performance thin-layer chromatography in order to correlate their structure and retention. Chromatographic systems were consisted of RP-18 or CN-silica as stationary phase, and binary water methanol, dioxane or acetone mixtures as mobile phase.

The investigated compounds possess the steroid moiety at one side of the tetraoxane ring and simply cycloalkane or isopropylidene group at the opposite side. Spirocycloalkane and isopropylidene moieties participate in hydrophobic interactions, polar tetraoxane ring acts as proton acceptor, and steroidal moiety participates in both hydrophobic and polar interactions (proton-donating and proton-accepting).

Based on the respective retentions, the lipophilicity of the investigated compounds was determined. Retention parameter, R_M^0, demonstrating the partition of the compounds between the non-polar stationary phase and water, was used to conduct a quantitative structure–retention (QSRR) study. Values of R_M^0, in a specific chromatographic system, were correlated with solute physicochemical properties, using LSER modeling and with theoretically derived molecular descriptors.

Principal component analysis (PCA) followed by multiple linear regression (MLR), in case of LSER model, and partial least squares (PLS), in case of modeling with molecular descriptors, have been used to select variables that best describe the behavior of the investigated compounds in chromatographic systems and to quantify their influences. Proposed models enable the prediction of behavior of congeners and understanding of their retention. The application of PCA allowed the classification of analytes with respect to their structural characteristics. The obtained models are statistically significant. The models indicate the importance of nonpolar properties of the solutes and their ability for hydrophobic interactions, as well as the importance of proton donating abilities, hydrophilic and π interactions pointing out on that way the possible separation mechanism in the studied chromatographic systems.

Acknowledgement: *This work has been supported by The Ministry of Education,Science and Technological Development of the Republic of Serbia, Grant No. 172008.*

BS-AS P11

Chemical characterization of normal wood of grey alder (*Alnus incana*) from Jošanička river basin, Kopaonik, Serbia

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Alnus incana (*Grey Alder* or *Speckled Alder*) is a species of alder with a wide range across the cooler parts of the Northern Hemisphere. *Alnus incana* is a light-demanding, fast-growing tree that grows well on poorer soils. In Europe, it is a colonist of alluvial land alongside mountain brooks and streams, occurring at elevations up to 1,500 metres. Various parts of alder were used in folk medicine as remedies for fever, hemorrhage and alcoholism. Despite the wide distribution of grey alder, the number of studies of the chemical compositions is low and fragmentary.

Herein, we present a detailed chemical analysis of grey alder normal wood collected from Jošanička river basin in Raška, Kopaonik (Serbia), 25 years old. The contents of cellulose, lignin and ash were determined as well as lipophilic and hydrophilic extractives. The contents of acetyl and methoxyl functional groups, uronic acids and pentosans also were investigated. The obtained results will be dicussed and compared with other alder species. In the study presented, the attention is focused on the fact that wood of grey alder, compared to the other deciduous tree species, contains an elevated amount of extractives.

BS-AS P12

Determination of phthalates esters in trans-boundary rivers

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The use of phthalates esters the industry has seen a worldwide increase, resulting with their presence in every segment of the environment. This research was focused on monitoring phthalate esters present in cross-border flows of Macedonia and their comparison to levels allowed in Macedonian and European legislation.

Six phthalates esters from the European priority list: dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate DBP), benzylbutyl phthalate (BBP), bis(2-ethylhexyl) phthalate (DEHP), di-*n*-octyl phthalate (DNOP) were monitored.

In the European legislation only DEHP is regulated with a maximum allowed value of 1.3 μg/L (average annual concentration), while the Macedonian legislation only regulates the total phthalates esters in first class of waters with maximum allowed concentration of 3 μg/L.

Research was performed with Agilent GC–qMS, while for confirmation of value Pegasus 4D GC × GC-TOF/MS was used. For calibration of the instruments standards were used with concentration in the range from 0.05 to 5.0 μg/L.

Analysis of the transboundary waters contamination with phthalates esters was conducted in a time interval of 10 months in the following locations: Lepenec River and Pčinja River on border with Serbia, Srumica River on border with Bulgaria, Vardar River and Eleska River on border with Greece. From the results obtained it can be noted that the transboundary pollution is still not alarming, values measured are below MCLs, and most significant part of measured phthalates esters is DEHP.

BS-AS P13

The substituent influence on the FTIR and UV spectral data of 2-substituted nicotinic acids

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The FTIR and UV spectra of a series of 2-substituted nicotinic acids were determined and the effect of compound structure and the applied solvents was studied. In order to analyze substituent influence, the absorption frequencies corresponding to the carbonyl group of the examined compounds were correlated with Hammett equation $\nu = \rho\sigma + h$, where σ the matching substituent constants for the absorption band of a carbonyl group of the specific compound, and ρ represents the sensitivity of the examined band to substituent effect. Furthermore, UV spectra were recorded in different solvent and again the absorption frequencies corresponding to the carbonyl group were analyzed, this time by Kamlet-Taft equation, in order to quantitatively present solvent influence. The Kamlet-Taft equation is given in the form $\nu_{max} = \nu_0 + s\pi^* + a\alpha + b\beta$ where ν_{max} is the absorption frequency, π^* is a measure of the solvent polarity, α represents the scale of solvent hydrogen bond donor acidities and β represents the scale of solvent hydrogen bond acceptor basicities.

BS-AS P14

Evaluation of strontium isotope abundence ratios in combination with isotope ratios of lead as a posible tool to study the geographical origin of tea

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Tea is one of the most popular drinks consumed by the human society [1]. In 2010, about 3.9 millions ton of tea was produced and consumed worldwide.

Tea price depends on its quality, flavour, and production area reputation [2]. Unfortunately, with the increase of the mobility and transport costs, the risk of fraud and unlabeling products with certified origin should be taken into account. Thus analytical methods are needed for economical fraud control. Geographical origin is especially important for tea [3].

The heavy isotope ratios can provide essential information for origin classification. Thus, isotope ratios strontium and lead, have some advantages over other factors in determining geographic origin. The isotopes of strontium and lead are hardly fractionated in the terrestrial ecosystem. There is no difference in the isotope ratio between parts of a crop, or between a crop and the exchangeable fraction in the soil, as long as the crop is grown under the same soil and water conditions.

Precise determination of strontium ($^{87}Sr/^{86}Sr$), lead ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$) isotope ratios in tea by MC-ICP-MS and ICP-MS has been used to investigate the correlation of this value from tea with its geographical origin and therefore the suitability of this parameter as a tool for food authentication, which is an important parameter of tea quality.

Results show that both isotopic systems of tea infusions show a relation to environmental factors that influence processes occurring during the growth of the tea plant.

The final results allowed discrimination of local provenances investigated in this study by superimposing results for strontium isotopic ratios and lead with literature data related to soil origin and exhibit the potential to proof authenticity of world teas. Thus, Pb and Sr isotopic ratios were able to classify tea samples from different regions.

References:

[1] Han,W.-Y., Shi, Y.-Z., Ma, L.-F. and Ruan, J.-Y. *Environ. Contam. Toxicol.* **75** (2005). 272–277.
[2] Tamara S. Pilgrim, R. John Watling, Kliti Grice. *Food Chemistry* **118** (2010) 921–926.
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BS-AS P15

Optimization of ICP-OES method for direct determination of trace elements in refined gold samples

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This paper presents method for direct determination of trace elements in refined gold samples. Contents of silver, copper, iron, palladium, zinc and platinum were determined by simultaneous inductively coupled plasma atomic emission spectrometer. In order to compare different calibration strategies, two sets of calibration standards were prepared. The first set was based on matrix matched calibration standards and the second was prepared without the addition of matrix material. Detection limits for matrix matching calibrations were higher for some elements than those without matrix matching [1]. In addition, the internal standardization method was applied and experiments indicated that indium were the best option as internal standard [2]. The results obtained for gold sample by matrix matching and matrix free calibrations were compared with results obtained by standard addition method. The accuracy of the methods were tested by performing recovery test. Recoveries for spiked sample were in the range of 90-115 %. The accuracy of the methods were also tested by analysis of certified reference material of high pure gold AuGHP1. The best results were achieved by matrix free calibration and standard addition method using indium as internal standard at wavelength of 230 nm.

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BS-AS P16

PM 10 concentration, trace elements content and Pb isotopic ratio in Belgrade and Novi Sad, Serbia

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Particulate matter (PM), which adversely affects human health, is commonly considered as one of the major factors contributing to urban air pollution problems. Many epidemiological and panel studies have shown an association between the levels of particulate matter in urban air and short-term cardiopulmonary effect [1]. In order to control PM levels, standards of PM concentrations are defined in the legislation of many countries [2]. Accessing the trace element content of PM 10 gives valuable information on the population exposure to toxic elements. The use of variations in stable lead isotope ratios has been recognized as a useful technique for characterizing sources of lead contamination and transport pathways of Pb in the environment. Therefore, lead isotopes have been introduced as “fingerprints” of environmental pollution [3].

In present study PM10 concentration was determined in two major Serbian cities, Belgrade and Novi Sad, in May 2012, using an automatic outdoor station for continuous atmospheric particulate monitoring according to EN 12341:1998 norm [4]. Trace elements (Pb, Cd, As and Ni) content was determined using Inductively coupled plasma mass spectrometer (ICP MS) according to EN 14902:2005 norm [5], while lead isotopic ratios were determined in isotope analysis mode using Agilent 7500ce ICP MS.

During the measurement period, there was no significant trend for distinctive pollution events in the PM10 concentrations. The mean value of PM 10 concentration for the Belgrade samples was 23.22±8.45 $\mu g/m^3$, while in the case of Novi Sad it was 29.34±8.42 $\mu g/m^3$. Trace elements concentrations were higher in Belgrade than in Novi Sad with large standard deviation for both cities. The mean $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios for both cities were 1.166 and 2.447, respectively, indicating the same source of Pb.

Acknowledgements: *The authors are grateful to the Ministry of Education, Science and Technological Development of the Republic of Serbia for the financial support (Project No. 172007).*

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BS-AS P17

Stoichiometric ratio and formation constants of aryldiketo acid complexes with Zn^{2+}

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Zn^{2+} Ion is an important cofactor in active sites of various enzymes (carbonic anhydrase, carboxypeptidase, histone deacetylase). Small organic molecules having zinc-binding groups are proven as inhibitors of such enzymes. 4-Aryl-4-oxo-2-butenoic acids (aryldiketo acids, ADK) and structurally related compounds were recently reported as selective inhibitors of class I carbonic anhydrase [1].
Interaction of the set 15 ADKs with Zn^{2+} was examined by UV/Vis spectrophotometry. Stoichiometric ratio and stability constants of ADK with Zn^{2+} under physiological conditions were determined (TBS: pH=7.34, I=0.15 M), using the mole-ratio method [2]. All complexes were formed with 1:1 (ADK : Zn^{2+}) molar ratio and comparable formation constants ($\log K_f$ ~ 5), Figure 1.

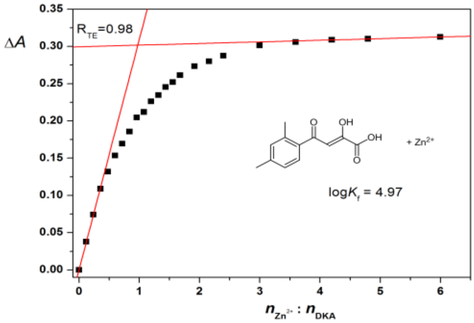

***Figure 1**. Mole-ratio plot for 2,4-di-Me ADK complex with Zn^{2+}.*

The effect of aryl ring substitution on complexation ability is discussed. Evaluation of inhibitory activity of reported compounds toward isozymes of human carbonic anhydrase is in progress, and obtained formation constants will be important guidance for the design of novel, more potent, and more selective inhibitors.

Acknowledgement: This work is supported by the Ministry of Education, Science and Technological Development of Serbia, under grant 172035.

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BS-AS P18

Structural characterization of tautomers of 3-Amino-5-hydroxypyrazole

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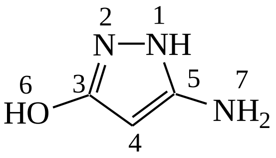
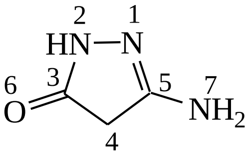
Pyrazole Ligand 3-Amino-5-hydroxypyrazole (**$C_3H_5N_3O$**) is structurally characterized and results have shown presence of two tautomers, tautomer A and tautomer B. [1].

Tautomer A (minor abundance)
^{1}H NMR (500 MHz, DMSO-d_6): δ 4.20 (s, H^4, 1H), 5.64 (s, H^7, 2H), 8.81 (br. s., H^1+H^6, 2H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 74.23 (C^4), 159.19 (C^3 or C^5), 170.72 (C^3 or C^5).

Tautomer B (major abundance)
^{1}H NMR (500 MHz, DMSO-d_6): δ 3.07 (s, H^4, 2H), 5.85 (s, H^7, 2H), 9.83 (s, H^2, 1H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 36.26 (C^4), 156.98 (C^5), 171.69 (C^3).



A



B

In the ^{1}H,^{13}C COSY (HSQC) diagram only two cross peaks were observed, indicating that the most abundant tautomer contains only one CH_2 group, whereas the second tautomer only one –CH= group. In addition, this implies that the relative abundance of the tautomers is 3:1.

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BS-AS P19

Solvent effects on the electronic absorption spectra of biologically active N^1-substituted 1,2,4-triazole derivatives using the *Catalán* solvent parameter sets

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The influence of a series of organic solvents on the UV spectra of investigated N^1-hetero-arylaminomethyl/ethyl-1,2,4-triazoles, was study by implementing solvatochromic theory.

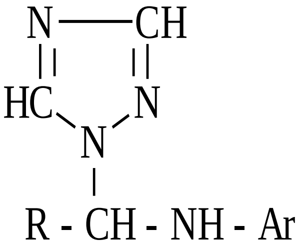

Figure 1. *Stucture of N^1-heteroarylaminomethyl/ethyl 1,2,4-triazole derivatives*

As a part of our efforts to interpret the effects of solvent polarity and hydrogen bonding on the absorption spectra of previously synthesized N^1-substituted 1,2,4-triazoles, the study design was based on the *LSER* concept using *Catalán* solvatochromic parameters: *SPP, SA* and *SB*.

Accordingly, by dividing the solvents into two groups (protic and aprotic) it was ascertained that improved solvatochromic three-correlation models for the group of protic solvents were obtained. The result show that the solvent effect on UV absorption spectra of investigated triazoles was very complex and strongly depends on the nature of the substituent in aminomethyl/ethyl moiety.

Moreover, the statistical evaluation of the models (R, SD, Q^2 and PRESS/SSY) showed satisfactory values.

BS-AS P20

Thermodynamic dissociation constants of some newly sunthezised *p*-nitro-*p*-substituted benzoilhydrazones in acid media

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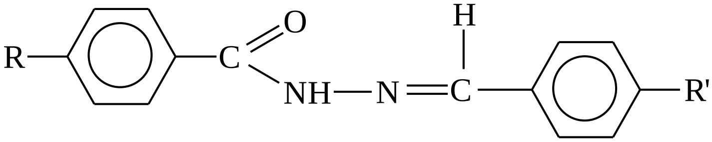
The importance and use of the hydrazones is due to biological activity that they possess which depends on the pH values of the media. Hence, the aim of our work was to follow the spectral behavior of some newly synthesized *p*-nitro-*p*-substituted benzoilhydrazones by the UV-Vis spectroscopic method in the acid media (7<pH<1).
The structural formulas of the hydrazones under study are:



R = –H, $-CH_3$, $-OCH_3$, –Cl, –OH R' = $-NO_2$

The spectra of the solution were studied and the position of the absorption maximum was defined in neutral and acidic media and the electronic transition were discussed, too. The equilibrium between the ionic forms in the solution was investigated in ethanol-water (1:1) mixtures. The two absorption bands (198 nm and 330 nm) appeared in the spectrum of all investigated hydrazones in neutral medium. The hipsochromic shift of the second absorption band was observed in acid solutions. It was confirmed that protonation process takes place in one step. The pH region of protonation ranges between 1.4 and 2.9.
Using the changes in the UV spectra which appear as a result of the protonation reaction the concentration dissociation constants were calculated. The pK_{BH^+} values were determined numerically from the absorbance values of the experimental and reconstructed spectra by characteristic vector analysis. Furthermore, the dissociation constants were determined graphically from the intercept of the dependence of log*I* on pH.
In order to obtain thermodynamic dissociation constants measurements were performed at ionic strength of 0.1, 0.25 and 0.5 mol/dm^3 ($NaClO_4$). There was a good agreement between the obtained pK_{BH^+} values of the investigated hydrazones and those of similar classes of compounds.

BS-AS P21

Evaluation of strontium isotope abundence ratios in combination with isotope ratios of lead as a posible tool to study the geographical origin of tea

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Ana Maria Josceanu*, Mariella Moldovan Feier**, J. Ignacio Garcia Alonso**,
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Tea is one of the most popular drinks consumed by the human society [1]. In 2010, about 3.9 millions ton of tea was produced and consumed worldwide.

Tea price depends on its quality, flavour, and production area reputation [2]. Unfortunately, with the increase of the mobility and transport costs, the risk of fraud and unlabeling products with certified origin should be taken into account. Thus analytical methods are needed for economical fraud control. Geographical origin is especially important for tea [3].

The heavy isotope ratios can provide essential information for origin classification. Thus, isotope ratios strontium and lead, have some advantages over other factors in determining geographic origin. The isotopes of strontium and lead are hardly fractionated in the terrestrial ecosystem. There is no difference in the isotope ratio between parts of a crop, or between a crop and the exchangeable fraction in the soil, as long as the crop is grown under the same soil and water conditions.

Precise determination of strontium ($^{87}Sr/^{86}Sr$), lead ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$) isotope ratios in tea by MC-ICP-MS and ICP-MS has been used to investigate the correlation of this value from tea with its geographical origin and therefore the suitability of this parameter as a tool for food authentication, which is an important parameter of tea quality.

Results show that both isotopic systems of tea infusions show a relation to environmental factors that influence processes occurring during the growth of the tea plant.

The final results allowed discrimination of local provenances investigated in this study by superimposing results for strontium isotopic ratios and lead with literature data related to soil origin and exhibit the potential to proof authenticity of world teas. Thus, Pb and Sr isotopic ratios were able to classify tea samples from different regions.

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BS-AS P22

Analysis of snow chemical composition based on IC method

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In last years, ion chromatography (IC) become the recommended method for air quality, proved to be a simple, fast, small volume sample demanding and reliable method for determination of anions and cations in aqueous samples.

The chemical composition of wet depositions was carried out from December 2012 to March 2013 in Bucharest, Romania [1]. Ten sampling sites were selected and 50 snow samples were collected in this period. The results of this study were compared to the earlier published data [2].

All samples were analyzed for pH, major anions (F^-, Cl^-, NO^{3-} and SO_4^{2-}) and major cations (K^+, Na^+, NH_4^+, Ca^{2+} and Mg^{2+}. The equipment used is an automated ion chromatograph ICS3000 Dionex gifted with conductivity detector for ion analysis. Most of the wet deposition samples prezented alkaline pH ($pH > 5.6$).

Measurements gived values within the 1.2 –21.7, 0.59 – 1.05, and 0.58–1.08 mg/L for Cl^-, NO^{3-} and SO_4^{2-} respectivel and 3.11 – 32.75, 0.47 – 12.39, 51.9 – 157.16, 4.29 – 27.4 and 23.81 – 162.5 mg/L K^+ , Na^+, Ca^{2+} , Mg^{2+} and NH_4^+ respectively and a realistic indicative of atmospheric pollution for many urban areas.

References:

[1] G. Han, Q. Wu, Y. Tang, *J. Atmos. Chem.* **115** (2011)
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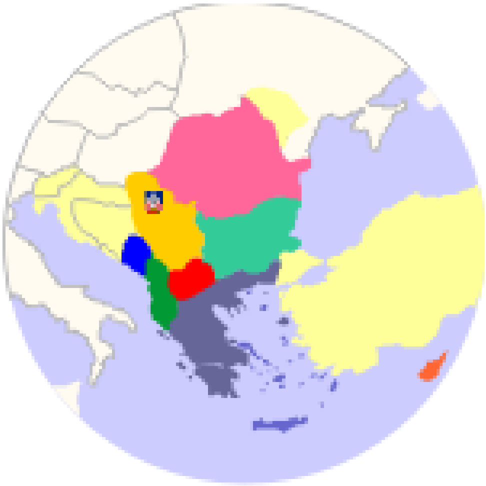

Catalysis

O 06 BS-Ca

Surface properties of TiO_2/ZnAl layered double hydroxide based coatings on brick substrates

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Intoduction

Surface of ceramic build materials are under constant exposure to outdoor conditions leading to inevitable degradation of their aesthetic and functional properties. Negative effect of organic, inorganic and microbial pollutants can be reduced or even avoided by application of proper protective coatings. For these purposes, photocatalytic active nanosized titanium-oxide has been extensively studied due to ability to remove organic and inorganic pollutants from material surfaces and provide hydrophilic surface necessary for the self-cleaning effect [1,2]. Photocatalytic potential of Zn-Al layered double hydroxides (LDH) was reported recently [3]. In order to increase the compatibility of the photocatalytic materials with ceramic substrates new inorganic-inorganic nanocomposite photocatalyst based on LDH associated to TiO_2 was studied.

Experimental

TiO_2/Zn-Al LDH nanocomposite was synthesized [4] and used for the preparation of the suspension which was deposited on the ceramic substrate surface by spay technique. Two different ceramic substrates were chosen: industrial made brick and handmade brick. Photocatalytic activity was evaluated by spectroscopic measurement of rhodamine B dye degradation under UV light irradiation. Due to the porosity of substrates, glycerol was used for the analysis of initial and static contact angle. The changes in contact angle value and surface water absorption were monitored before and during the exposure to UV irradiation in order to evaluate any difference due to photo-induced hydrophilicity.

Results and conclusion

The results showed significant photocatalytic activity (ca. 19% for the coated handmade brick and 14% for the industrial brick after 3.5h of UV irradiation) and development of photo-induced hydrophilicity. Greater decrease of contact angle value was observed for the coated handmade brick, followed by higher overall photocatalytic activity. The study revealed that TiO_2/ZnAl layered double hydroxide based coatings present promising materials for the design of protective photocatalytic coatings on ceramic substrates.

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O 07 BS-Ca

The effect of the Fenton process on the characteristics of natural organic matter and arsenic removal from groundwater

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The main objective of this research was to study the effects of Fenton's process on the characteristics of natural organic matter (NOM) and the removal of arsenic (As) from groundwater with a high content of NOM (10.4±0.2 mg/L DOC). The effects of pH (pH 5.5 and 6.0) using 0.25 mM Fe(II) and a molar ratio of Fe(II):H_2O_2 of 1:10 at different reaction times (1-30 min) were investigated, whereby NOM was more efficiently reduced by Fenton's process at pH 5.5 (up to 48% DOC removal) than pH 6.0 (up to 30% DOC removal). NOM removal by Fenton's process at pH 6.0 and coagulation alone using iron(III) salts [1] was nearly the same, indicating that at this pH, the oxidation step of Fenton's process was inhibited due to iron precipitation, with NOM removal occurring mainly due to coagulation. Further investigations were therefore performed at pH 5.5 and the results compared with our previous research conducted at pH 5 [2]. Using different concentrations of reagents (0.10-0.50 mM Fe(II) and a molar Fe(II):H_2O_2 ratio of 1:5-1:20), DOC reductions of 10-55% were achieved, where an Fe(II) dose of 0.25 mM and Fe(II):H_2O_2 of 1:5 proving most effective. Higher molar ratios of Fe(II):H_2O_2 (1:20) and 0.25 mM Fe(II) appeared to be the most effective in decreasing the trihalomethane formation potential (up to 80% THMFP), probably due to the favoured oxidation mechanism with OH radicals and precipitation. Similar results were obtained in our previous research at pH 5.0, whereby Fenton's process at pH 5.0 proved to be more effective in the removal of DOC and THM precursors content (up to 80% and 97%, respectively, [2]) than at pH 5.5. Results of NOM characterisation showed that applying the Fenton process at pH 5.5 results in significant changes in the NOM structure. The humic acid fraction was completely removed, the fulvic acid fraction content decreased and the contribution of residual hydrophilic NOM increased by up to 79% in treated water. The residual hydrophilic acid fraction was the most reactive NOM fraction in terms of THMs formation. Under all the investigated Fenton's process conditions, no carcinogenic bromate formation was observed, and As contents were reduced from 110 µg/l in the raw water to <5 µg/L. Fenton's process at pH 5.5 showed high efficiency in the removal of As and THM precursors from water. However, the high residual of total NOM (about 5 mg/L DOC) and their reactivity requires a combination of Fenton's process with other technologies in order to achieve healthy safe drinking water.

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O 08 BS-Ca

Optimization by the simplex method of the separation of nicosulfuron and its photodegradated intermediates by high-performance liquid chromatography

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Nicosulfuron (1-[4,6 dimethoxypyrimidin-2-yl]-3-[3-dimethylcarbamoyl-2-pyridylsulfonyl]-urea) is a sulfonylurea herbicide that has been used successfully for weed control in corn [1]. Sulfonylurea herbicides have become very popular worldwide because of their high selectivity, low application rates, low mammalian toxicity and low persistence in the environment [2]. However their natural photodegradation can bring formation of intermediates potentially more toxic and stable than the precursor herbicides [3]. Therefore it is necessary to optimize the HPLC method to detect starting compound and all the intermediates.

The aim of the optimization is to find out the optimal parameters for complex system such as analytical methods. The parameters that we need to determine are the values that describe the system. The simplex is one of the most simple and general optimization method which is used to predict the experiments that in quickest way lead to an optimum [4].

In the present study we have performed the photocatalytic degradation of nicosulfuron in aqueous TiO_2 suspensions irradiated with UV light in order to get the mixture of nicosulfuron and formed intermediates. Simplex optimization of a high-performance liquid chromatography has been developed for TiO_2 suspension with irradiation time of 2 minutes, because for this time irradiation in the system appears the most intermediates. After the organic solvent had been chosen (acetonitrile), an isocratic analysis was performed with three parameters of optimization: column and oven temperature, percentage of acetonitrile and flow rate. The optimal conditions were determined by the simplex and in order to measure them a Chromatographic Response Function was chosen. With the optimal condition the resolution of chromatograms was better and time of analysis was decreased.

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O 31 BS-Ca

Non-innocent character of oxyanions in ruthenium metathesis catalysts

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The synthesis, characterization, reactivity and selectivity of six novel ruthenium-based metathesis catalysts containing oxyanions as ligands are described and are presented through series of complexes with carboxylate ligands, as well as the nitrate ligand. A drop in chemoselectivity and/or reactivity in alternating ring opening metathesis of norbornene and cyclooctene for certain catalysts is observed, while other catalysts show the expected activities and chemoselectivities. An explanation of this observation lays in a chelating effect of oxyanion ligands in these complexes. By comparison of selectivity and reactivity in copolymerizations with NMR and X-ray structures, we have uncovered correlations which serve as predictive tools for catalyst design. We document the negative effect of a chelating oxyanion ligand on the rate and selectivity in AROMP, and introduce NMR and crystallographic indicators which correlate with the degree to which the negative effects actually appear[1].

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BS-Ca P01

Development of new catalytic system based on nanostructured perovskite for DeNOx process

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Diesel engines emit large quantities of particulate matter (called PM) and nitrogen oxides (NO*x*), both precursors of photochemical smog. Growing alarms on health effect and pressure to fulfil the governmental directives for the reduction of pollutants emissions from diesel engines are paving the way for the development of tailored treatment systems. These cannot be accomplished by engine modifications, fuel pretreatments or simply better tuning of the combustion process; thus a convenient way of treating diesel off-gases is needed. [1]

Perovskite type oxides of general formula ABO_3 where A and B are usually rare earth, alkali earth, alkali or other large ions and transition metal cation respectively are less expensive, thermally more stable, diverse physicochemical properties, increase thermal stability of the support, store and release oxygen under conditions fluctuating between oxidizing and reducing than noble metal used in catalytic converter to reduce emission from diesel engines. [2]

This paper focused on the optimisation of the operating parameters of the synthesis route involving templating methods in order to adjust the textural properties according to the selected application. Indeed, the porosity plays an important role in determining the efficiency of the catalysts in the course of the reaction, because an optimal pore size distribution will favour the diffusion of the reactants and products inside the pore structure improving the overall performances.

When obtaining supported perovskites, two factors concur: the nature of the support and the preparation method chosen for active phase deposition. Unfortunately, the most common and largely accessible supports such as Al_2O_3 and SiO_2 are reactive towards the elements contained in the perovskites, resulting in catalytically inert compounds such as spinnels. In our work we will use nanostructured material such as diatoms with special properties for obtaining supported perovskites.

Supported $FeCuO_3$ perovskites will be obtained by wet impregnation of different diatoms with a solution prepared from Fe and Cu nitrates, using citrate route. The obtained material will be calcined at 600^0C for 5 h.

A panel of various physico-chemical techniques will be implemented for bulk and surface characterisations (TGA-DTA analysis, X-ray diffraction, Raman spectroscopy, IR spectroscopy, BET surface measurements).

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BS-Ca P02

Activity of DPU-Ni/D hydrogenation catalysts prepared by urea method

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Nickel catalysts supported on diatomite (Ni/D) were prepared by deposition-precipitation urea (DPU) method [1]. The precipitation of Ni(II) phase onto diatomite surface was performed under various deposition-precipitation times. The catalyst precursors prepared with different nickel loading were then subjected through preparation steps including drying, reduction and passivation under the same conditions.

Characterization of textural, structural and reducible properties was carried out using following techniques: N_2-physisorption, Hg-porosimetry, XRD, IR, TG-DTG and TPR.

The activity of DPU-Ni/D catalysts was tested in the reaction of hydrogenation of soybean oil. This reaction was performed in a three-phase slurry reactor, under conditions described in our previous paper [2].

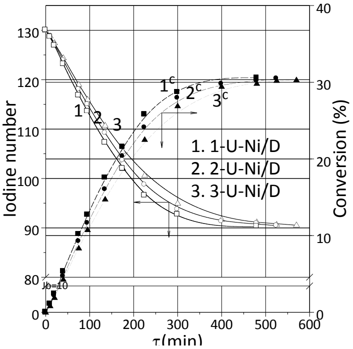

Fig. 1.*Iodine number and Conversion* vs. *hydrogenation time*

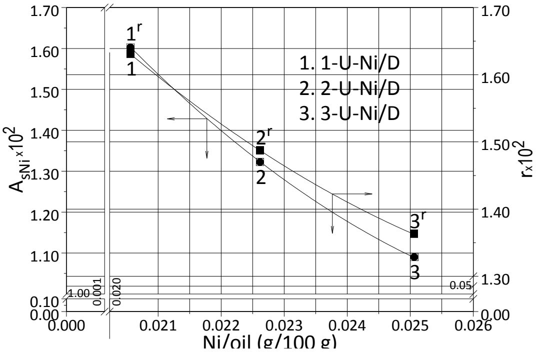

Fig. 2. *Specific activity* (A_{sNi}) *and hydrogenation rate* (r) *vs Ni loading*

Figures 1 and 2 show the activities of the 1-U-Ni/D, 2-U-Ni/D and 3-U-Ni/D in catalytic test reaction of soybean oil hydrogenation. For hydrogenation reaction the highest activity was observed for the catalyst sample 1-U-Ni/D with the lowest nickel loading. The activity of catalyst samples increased in the following order: 1-U-Ni/D > 2-U-Ni/D > 3-U-Ni/D.

An observed trend of increasing activity with decrease of Ni loading is in good correlation with the results obtained by the characterization of the catalyst surface and, in particular, with reducible characteristics of prepared DPU-Ni/D catalyst samples.

Acknowledgment: *This work is supported by the Ministry of Education and Science of the Republicof Serbia (Project III45001).*

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BS-Ca P03

Pretreatment influence on CaO catalyst activity in biodiesel synthesis

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Biodiesel has gained international attention as an alternative fuel due to its high degradability, low toxicity and emission. It is successfully produced by transesterification, mostly using homogeneous catalysts. However, general advantages of heterogeneous processes direct new investigation towards heterogeneous catalysis. High specific surface area, strength and population of basis sites are characteristics generally attributed to heterogeneous catalyst of high activity, mainly solid metal oxides. In this work phisico-chemical properties of CaO were correlated to its activity.

CaO catalyst was calcinated in a temperature range 700-1100 °C and characterized by means of phase composition (XRD), textural properties (LTNA) and also strength and number of active basic sites (temperatures of CO_2 desorption in TPD regime and area under the peak of the TPD). Transesterification reaction was performed in a glass laboratory batch reactor equipped with a magnetic stirrer and a cooler. Methanol to oil ratio (6/1 mol), catalyst loading (1 %mas) and reaction time (2h) were kept constant, as well as reaction temperature (65 °C) and rate of mixing (625 rpm). Catalyst activity is determined by quantity of methyl-esters (M-E) formed in the reaction, and verified by gas-chromatography analysis.

Phase analysis shows early CaO formation and its fraction increases following calcination temperature. There is a decreasing trend in CO_2 desorption temperatures in the calcinations range 700-900 °C (Table 1). However, the strongest basic sites coincide with the catalyst calcined on 1000 °C, related to the highest activity as well.

Table 1. Strength of basic sites of CaO and its activity in reaction

Calcination Temperature, °C	TPD of CO_2, °C		Surface area, m^2/g	Relative area under TPD	Mean pore diameter, nm	Yield of M-E, %
700	528	582	3.5	0.67	18.2	73.2
800	520	558	8.3	0.68	18.3	-
900	507	544	2.4	0.76	14.3	43.8
1000	614	718	2.3	0.76	12.7	84.5
1100	538	599	2.9	1.0	8.4	60.7

Acknowledgements: *The financial support by Ministry of Education and Science of Serbia (Project 172059) is appreciated.*

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BS-Ca P04

Kinetic study of phenilselenoetherification of α-terpineol, cineol precursor

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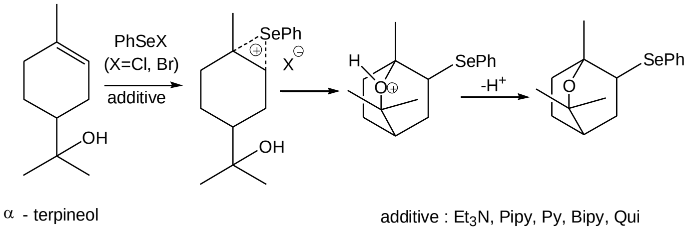
Cyclofunctionalizations of alkenols

Unsaturated alcohols, with convenient position of a double bond and a hydroxyl group, undergo intramolecular cyclization process, giving THF and THP ring type products. By using phenilselenohalides as reagents, these cyclizations occur very fast, under mild conditions, with the added benefit of easy PhSe-group removal, and also manifesting in high yields of cyclic products [1]. The importancy of cyclic ethers obtained in this way is shown in their vast presence in natural products and pharmaceutical compounds, as well as in their biological activity and synthetic value. Important natural product, cineol, can easily be obtained by phenylselenoetherification of α-terpineol [2]. In order to further improve this reaction, we felt necessary to examine the kinetics and mechanism under which the intramolecular cyclizacion occur.

As it can be seen from the Scheme, this is the two step mechanism, where the nucleophilic attack of pendant hydroxil group is a rate determing step.



additive : Et_3N, Pipy, Py, Bipy, Qui

The mechanism of phenylselenoetherification of α-terpineol using PhSeCl and PhSeBr as reagents, some Lewis bases (triethylamine, pyridine, pipyridine, quinoline, 2,2′-bipyridine) as catalysts, in THF as a solvent was examined through kinetic study by UV–Vis spectrophotometry, under *pseudo*-first order conditions, where we determined rate constants for the cyclization reactions (k_2) and competitive, addition reaction (k_1). The obtained values for rate constants k_2 show that the reactions with PhSeBr are slower then those with PhSeCl. The reaction with piperidine is the fastest one. The presence of base catalyst supressess the competitive reaction almost completly ($k_1 \approx 0$). It is found that these reactions follow the mechanism of bimolecular nuclephile substitution S_N2 pathway, which is in accordance with our previous experimental findings [3].

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BS-Ca P05

Photocatalytic degradation of alprazolam using ZnO

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Benzodiazepines are one of the most prescribed pharmaceuticals, which are frequently detected in the environment [1]. Alprazolam (8-chloro-1-methyl-6-phenyl-4*H*-[1,2,4] triazole[4,3,-α]-[1,4]-benzodiazepine, Fig. 1) is one of the fifth generation benzodiazepines. It is a benzodiazepine mainly used to treat anxiety disorders. On a short time basis it is used to palliate symptoms of anxiety or anxiety associated to symptoms of depression [2,3]. Because of their frequent use and chemical stability, there is a strong need for finding efficient methods for their removal and transforming to the products that are not harmful to the environment.

In the present study photocatalytic degradation of alprazolam was investigated in aqueous ZnO suspensions irradiated with UV light. A 125 W medium-pressure mercury lamp was used as the radiation source. The degradation kinetics was monitored by HPLC-DAD.

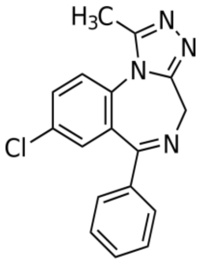

Fig. 1. Structural formula of alprazolam [1]

The efficiency of the photocatalytic degradation of alprazolam in the aqueous ZnO suspensions was examined as a function of the ZnO loading. Bearing in mind that the solution pH is an important factor in the heterogeneous photocatalytic reactions since it influences of photocatalysts surface charge and the size of aggregates of its particles, it was been subject of our investigation. In order to enhance the formation of hydroxyl radicals and also inhibit e^{-}-h^{+} recombination, the effects of $KBrO_3$ and H_2O_2 on the kinetics of photocatalytic degradation of alprazolam was investigated. To check whether the heterogeneous photocatalysis take place via hydroxyl radicals, ethanol and methanol were added to the reaction mixture containing alprazolam and ZnO at 25°C. The results show that alcohols inhibit degradation of alprazolam.

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BS-Ca P06

Improvement of pozzolanic mortars by application of TiO_2/ZnAl layered double hydroxide based protective coating

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Introduction

Design and application of self-cleaning photocatalytic active coatings on surfaces of immovable cultural heritage objects is important since it represents a possibility to eliminate or suppress the problems related to the long-term exploitation and inevitable deterioration of these surfaces due to their exposure to outdoor conditions. The study was focused on the development of innovative environmental friendly mortars using low grade clay materials and industrial by-products with synergetic action of photocatalytic and hydrophilic properties for the protection of immovable cultural heritage objects. Based on the results of historical mortar characterizations, pozzolanic mortars were designed taking into account both waste management and the existing conventions in the area of cultural heritage [1]. Hydrophilic photocatalytic active coatings were developed and examined. Photocatalytic active inorganic nanocomposite coating based on TiO_2 and Zn-Al layered double hydroxides (LDHs), were prepared with the idea to increase the overall activity of TiO_2 by association with LDHs, as well as to increase the compatibility of photocatalyst with pozzolanic mortar.

Experimental

Nanocomposits based on TiO_2 and Zn-Al layered double hydroxides (LDHs) were synthesized [2]. Photocatalysts were deposited as suspension by spray technique on the mortar surface as coatings. Rhodamine B degradation under UV light irradiation was selected as test reaction for the evaluation of photocatalytic activity. Surface properties such as roughness, micro-hardness, surface energy (initial and static contact angle) were measured for the referent mortar without photocatalytic coating and for the mortar with coating.

Results and conclusion

The comparative study showed that the application of protective coating based on inorganic-inorganic nanocomposites on pozzolanic mortar surface improves surface properties of pozzolanic mortars since it initiates photocatalytic activity and photo-induced hydrophylicity.

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BS-Ca P07

Pore surface fractal analysis of Mg^{2+} doped alumina obtained by sol-gel method

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Mesoporous alumina is widely used as catalyst supports, because their high specific surface areas, surface property and crystalline structure are important in the field of various catalysis [1,2]. Influence of annealed temperature on the pore structure and surface fractal dimension of Mg^{2+} doped alumina prepared by sol-gel method was investigated. The pore structure is evaluated by BET method based on nitrogen adsorption isotherms. Mahnke and Mögel method [3] is used to determine the pore surface roughness of alumina samples. The results of sorption analysis show that the samples annealed at 500 °C and 700 °C exhibited a typical type - IV isotherms with hysteresis loops of the H2 type, which were typical of mesoporous materials and slit shaped pores. After annealing at 1000 °C samples are poses type - II isoterms, a representative of mesoporous material with narrow pores. The mesoporosity values of annealed samples show a slight decrease before 700 °C and monotonic decrease at higher temperatures. The changes of porous structure are accompanied by the phase transformation of γ-Al_2O_3. At higher temperatures (1100 °C) the formation larger pores due to the collapse of the pores with shrinkage of the material structure resulted in a strong increase in crystallite size and decrease of surface area and pore volume. Smoothing and sintering effects also contributed to the general decreasing trend of surface fractal dimensions with increasing temperature from 1000 °C to 1200 °C. The slight decrease in valeu of surface fractal dimensions from 2.19 to 2.07, may be ascribed to the dispersion of Mg^{2+} into the narrow pores of alumina and then to the smoothing out of the surface.

Acknowledgments: *This work was supported by the Ministry of Education and Science of the Republic of Serbia (Projects number III 45001 and ON 172015).*

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BS-Ca P08

Synthesis and characterization bimetallic nanoparticle Au-M (M = Pd, Pt, Rh) by alkaline polyol method

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Nanoparticles are very interesting materials from scientific and practical points of view as well as with numerous applications in electronic, catalytic, biomedical or sensor fields. Several preparation methods with various complexity degrees are currently available. One of the most convenient and versatile procedure of synthesis is the so called ‘polyol method’.

In this work, well-dispersed, uniform bimetallic Au-M nanoparticles, where (M = Pt, Pd, Rh), protected with PVP have been synthesized by a modified protocol alkaline polyol method. To control the particles growth and avoid the particle agglomeration as well as to obtain narrow size distribution, PVP (polyvinyl pyrrolidone) was used as protective polymer. The obtained nanoparticles were characterized by various methods (TEM, XPS, and XRD) to elucidate the relationship between morphology and preparation variables. The structure of the nanoparticles was of core-shell type and the average nanoparticle diameter ranged between 1 and 8 nm.

The final structure of bimetallic nanoparticles was found to be determined by the morphology particles resulted in the first reduction step.

Finance support by grants INTEGRATREAD 100/2012 and BICLEANBIOS 46/2012 is greatly acknowledged.

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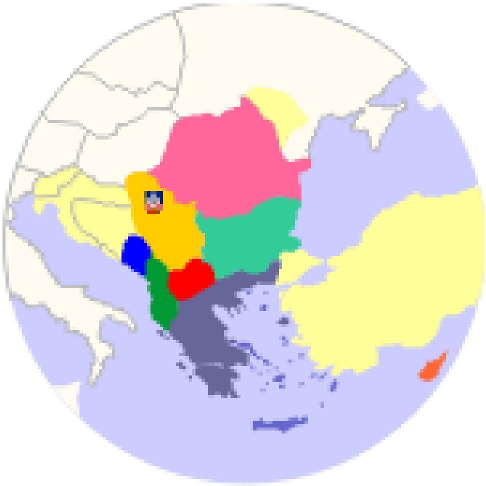

Chemical Biology

O 09 BS-CB

Antimicrobial activity of three square-planar complexes of Ni(II) with ethyl (2*E*)-2-[2-(diphenylphosphino)benzylidene]hydrazinecarboxylate and monodentate pseudohalides

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Three new square-planar Ni(II) complexes [NiL(OCN)] (**1**), [NiL(NCS)] (**2**) and [NiL(N_3)] (**3**) with the condensation derivative of 2-(diphenylphosphino)benzaldehyde and ethyl carbazate (HL) have been synthesized (Fig. 1). The structures of complexes were determined by elemental analysis, IR and NMR spectroscopy and X-ray crystal analysis. Antibacterial and antifungal activities of the complexes were studied using disc-diffusion method. The ligand and all the complexes showed a significant activity at 100 µg/discs against yeast species, *C. albicans* and *S. cerevisiae*, the complexes being more active. Antifungal effects of the complexes to *C. albicans* were more pronounced than either a nickel salt or salts containing the corresponding anionic ligand. The complexes and the ligand were also active to some plant pathogenic fungi. Antibacterial activity was tested against seven strains of Gram-positive and five strains of Gram-negative bacteria. Contrary to antifungal effects the antibacterial activity was poor, the ligand and two complexes being inactive, while the activity of the azido complex was lower than the activity of the corresponding nickel salt.

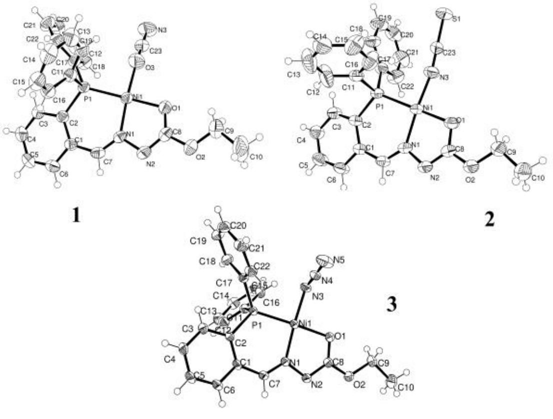

*Fig. 1. ORTEP diagram of complexes **1, 2** and **3***

Acknowledgement. *Financial support of the Ministry of Education and Science of the Republic of Serbia (Grant OI 172055).*

O 10 BS-CB

Crystal structure of $\{[Pt(en)Cl]_2(\mu\text{-}pd)\}Cl_2$ and ^1H NMR investigation of the hydrolytic reactions between L-methionine- and L-histidine-containing peptides and this binuclear platinum(II) complex

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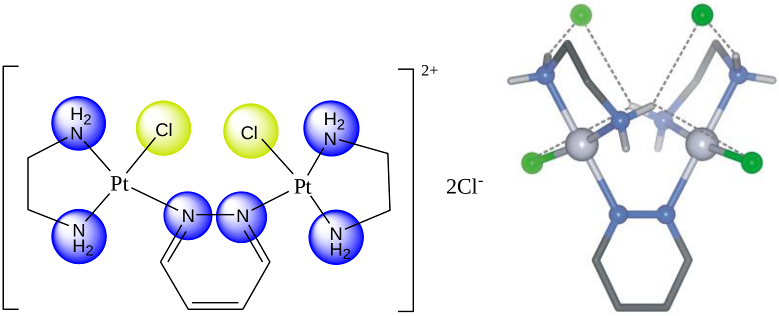
In the present study we report the synthesis and the X-ray characteristics of the binuclear $\{[Pt(en)Cl]_2(\mu\text{-}pd)\}Cl_2$ complex (en is ethylenediamine acting as a bidentate ligand; pd is bridging pyridazine ligand). X-ray results demonstrate that the needed support for pyridazine bridging, usually provided by bridging units coordinated to a metal center, comes in this crystal structure from supramolecular NH...Cl...HN interactions.



$\{[Pt(en)Cl]_2(\mu\text{-}pd)\}Cl_2$

This complex was converted into the corresponding aqua complex, $\{[Pt(en)(H_2O)]_2(\mu\text{-}pd)\}^{4+}$, and ^1H NMR spectroscopy was applied for comparison of its catalytic activities in the hydrolysis of the *N*-acetylated L-methionylglycine (Ac-L-Met–Gly), L-histidylglicine (Ac-L-His–Gly) and L-methionyl-glycyl-L-histidyl-glycineamide (Ac-L-Met-Gly-L-His-GlyNH$_2$). All reactions were performed in the pH range 2.0–2.5 with equimolar amounts of the Pt(II) complex and the corresponding peptide in D_2O as solvent and at 37 °C. The reactions of the $\{[Pt(en)(H_2O)]_2(\mu\text{-}pd)\}^{4+}$ complex with the Ac-L-Met–Gly, Ac-L-His–Gly and Ac-L-Met-Gly-L-His-GlyNH$_2$ peptides under the previously mentioned experimental conditions were remarkably selective in the cleavage of the amide bond involving the carboxylic group of methionine in the side chain. These results are an important step in the study of the regioselective cleavage of peptides and proteins and in the development of new platinum(II) complexes as artificial metallopeptidases.

Acknowledgements*. This work was funded in part by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172036).*

BS-CB P01

Structure–activity relationship of styryl lactones related to (+)-and (–)-goniofufurone

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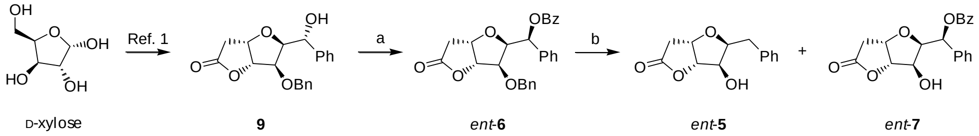
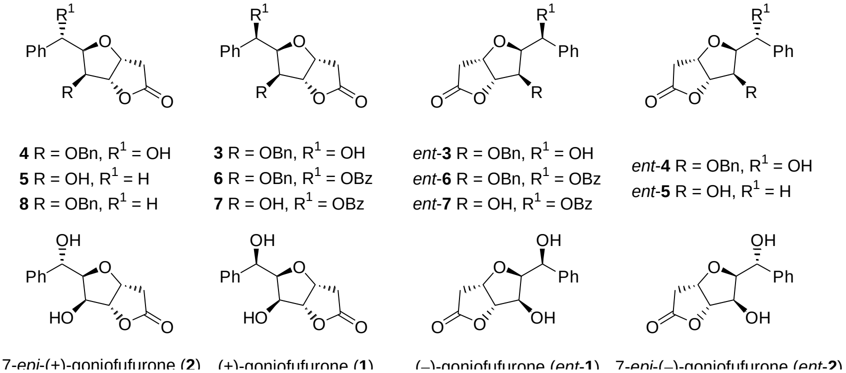
(+)-Goniofufurone (**1**) and 7-*epi*-(+)-goniofufurone (**2**) are natural styryl lactones, while (–)-goniofufurone (*ent*-**1**) and 7-*epi*-(–)-goniofufurone (*ent*-**2**) are their opposite enantiomers, which were obtained by synthesis. All these compounds show a notable cytotoxic activity *in vitro*. Herein we want to report the synthesis of two novel analogues of *ent*-**1** (*ent*-**6** and *ent*-**7**), as well as the results of their biological activity. Also, we will present results of antiproliferative activity and structure–activity relationship (SAR) of **1**, *ent*-**1**, **2**, *ent*-**2** and analogues (**3** – **8** and *ent*-**3** – *ent*-**7**) that were previously synthesized in our laboratory. The results indicate that, in more cases, the (+)-goniofufurone mimics show a more potent cytotoxicity than the opposite enantiomers of (–)-goniofufurone series. Also, introduction of a deoxy function at the C-7 position increases the antiproliferative activity of the analogues in both series of enantiomers.



Sheme 1. Reagents and conditions: (a) BzOH, Ph3P, DEAD, anh. THF, 0 °C for 0.5 h, rt for 2 h, 48%; (b) H2, 10% Pd/C, EtOAc, rt, 72 h.



Sheme 2. Structures of goniofufurone, 7-epi-(+)-goniofufurone and analogues.

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BS-CB P02

Cytotoxic activity and thermal analysis of some binuclear Cu(II) complexes with *N,N',N",N'"*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc) without or with simple anions as co-ligands

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Seven cationic binuclear Cu(II) complexes with *N,N',N",N'"*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraaza-cyclotetradecane (*tpmc*) without or with some co-ligands (F^-, Cl^-, Br^-, I^-, NO_2^-, $2SCN^-$) and ClO_4^- as counter ions were prepared as described [1a-1c]. They were evaluated for *in vitro* cytotoxic activity against 3 cell lines with cisplatin (cis-DDP) as a referent compound, together with the free ligand *tpmc*, $Cu(ClO_4)_2{\cdot}6H_2O$, simple salts of the corresponding anion and the solvent DMSO as a controls (standard MTT assay [2]). The free *tpmc*, $Cu(ClO_4)_2{\cdot}6H_2O$ and solvent DMSO were inactive, whereas F^-, Cl^-, Br^- and SCN^- simple salts showed weak or moderate activity in some cases. Contrary, the activity of the complexes were ~4-5 times higher than the corresponding simple salts of the co-ligands. Especially active was [Cu$_2$*tpmc*]$(ClO_4)_4$. The detected IC50 values were discussed in respect of the geometry of the complexes, the conformation of macrocyclic ligand *tpmc* (boat/chair), steric hindrance, magnetic properties [1d], as well as the nature of co-ligand. Thermogravimetric measurements were carried out by simultaneous TGA/DSC equipment in N_2 atmosphere and temperature range up to 500 °C. In all complexes the decomposition is accompanied by highly exothermic effect primarily due to the presence of ClO_4^-. In complexes with halide bridged ligands the exothermic effect and the rates of decomposition decreased with decreasing electronegativity of the halide. Starting from the Br^- complex the fragmentation of the ligand is observable. In the complex with $2SCN^-$ (pseudo-halide) the decomposition steps are clearly separated. The thermal stability of the complexes can also be related to their stability constants and is in accordance with Pearson's Hard and Soft Acids and Bases (HSAB) principle [3].

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BS-CB P03

Quantitative structure-activity relationship study of some antipsychotics by multiple linear regressions

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The retention behavior and lipophilicity parameters of some antiphychotics were determined using reversed-phase thin layer chromatography. The lipophilicity has a significant impact on the absorption, distribution, metabolism, and excretion of compounds. Quantitative structure-activity relationships studies have been performed to correlate the molecular characteristics of observed compounds with their retention as well as with their chromatographically determinated lipophilicity parameters. An effect of different organic modifiers (acetone, tetrahydrofuran, and methanol) has been studied. The retention of investigated compounds decreases linearly with increasing concentration of organic modifier. Obtained results are in agreement with polarity of applied organic modifiers as well as structure of investigated compounds. The chemical structures of the antipsychotics have been characterized by molecular descriptors which are calculated from the structure and related to chromatographically determinated lipophilicity parameters by multiple linear regression analysis. Established QSAR model for acetone as organic modifier is excellent. For this model PRESS/SSY value is smaller than 0.1. Established model gives us the possibility to gain insight into factors responsible for the retention as well as lipophilicity of the investigated set of the compounds. Also, this study provide good information about pharmacologically important physico-chemical parameters of observed antipsychotics relevant to variations in molecular lipophilicity and chromatographic behavior. A very advantageous feature of established models is that it allows us to understand chromatographic behavior of novel, not yet synthesized compounds, solely from their structural descriptors, and estimate lipophilicity for similar compounds.

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BS-CB P04

Anti-hydroxyl radical activity of the volatile natural products of the freshwater bryozoan *Hyalinella punctata* (Hancock, 1850)

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The volatiles from the freshwater bryozoan *Hyalinella punctata* (Hancock, 1850) were isolated (hydrodistillation, Clevenger apparatus), identified (gas chromatography /GC/ and gas chromatography-mass spectrometry /GC-MS/) and *in vitro* screened (electron paramagnetic resonance spectroscopy /EPR/ and fluorescent spectroscopy) for anti-hydroxyl radical activity. The samples **1** and **2** of *H. punctata* were collected from Danube river in Belgrade, Serbia in November 2011 and May 2012, respectively. The main components of the sample **1** /2-ethyl-1-hexanol (34.89%), *n*-dodecanol (20.18%) and hexanal (7.98%)/ and the sample **2** /2-ethyl-1-hexanol (27.91%), 7-tridecanol (22.69%), 1-hexadecanol (11.04%) and hexadecanal (6.99%)/ were relatively similar. However, the sample **2** was consisted of more chemical constituents in comparison with the sample **1** (28 and 22, respectively). EPR measurements, based on spin-trapping method using DEPMPO (5-diethoxyphosphoryl-5-methyl-1-pyrroline-N-oxide) showed significant antiradical activity of the both samples (75% and 87%, respectively). On the other hand, fluorescence emission intensity, using APF /3'-(*p*-aminophenyl) fluorescein/ as the probe positively correlated to hydroxyl radical production, dropped to 3.36% and 3.04% of the initial intensity, respectively. The generation of other types of free radicals in reaction with hydroxyl radical was not observed. According to the best of our knowledge, this is the first report of volatile compounds of any freshwater bryozoan species. Simple organic chemicals of low molecular mass such as alcohols, aldehydes and ketones seem to be characteristic for the volatiles of this animal phylum. Further investigations will focus on headspace GC analysis, comparative isolation (Clevenger apparatus versus Likens-Nickerson apparatus) and other types of free radicals including reactive nitrogen species. New antioxidants possibly identified could be considered as leads for development of novel drugs or food supplements.

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BS-CB P05

Complexes of Ru(II) with N-alkylphenothiazines – LDH enzyme activity

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Lactate-dehydrogenase (LDH) is a cytoplasmatic enzyme present in essentially all major organ systems. Its role in metabolism is to catalyse the oxidation of L-lactate to pyruvate as the final step in the metabolic chain of anaerobic glycolysis. The enzyme is formed of four peptide chains of two types: heart (H) subunit or muscle (M) subunit predominanted in the respective tissues and it has five different isoenzymes which catalyse the same biochemical reaction and are more or less organ specific. The isoenzymes are separable electrophoretically. The subunit compositions of the five isoenzymes in order of decreasing anodal mobility in an alkaline medium are: LDH-1 and LDH-2 (found primarily in heart and red blood cells), LDH-3 (lung), LDH-4 (kidney and skeletal muscle) and LDH-5 (dominantly in liver).

Ruthenium complexes are very active compound biologically and in this point we are investigated the effect of two Ru(II) complexes on the activity on LDH isoenzymes in rat blood. The general formulae of complexes are TF.2H[$RuCl_3(DMSO)_3$] (**1**) and TF.2H[$RuCl_3(\eta^6$-*p*-cymen)] (**2**), where TF.2H is protonated trifluoperazine, both prepared and characterized in our laboratory [1,2]. Also, these complexes exhibited antiproliferative activities on a four human carcinoma cell lines, as well as on the antioxidant enzyme activities (superoxide dismutase and catalase), level of nitrite production and erythrocytes malondialdehyde in rats blood under physiological conditions [1,2]. In continuation of our research, the effect of three different doses (0.4, 4.5 and 90.4 μM/kg bw) of complexes **1** and **2** are investigated on LDH isoenzymes activities in rats blood, under physiological conditions. Complex **1** decreases activity of LDH_2 isoenzyme in all applied doses, while activities of the LDH_1 and LDH_4 applied with 4.5 μM/kg bw of complex **1** are increased. The activity of LDH_1 and LDH_2 isoenzymes are descreased in all applied doses of complex **2**, while the effect of this complex on LDH_4 and LDH_5 shows increase of their activities. Results of LDH isoenzymes activities show different sensitivity depending on the applied concentration of the complexes **(1)** and **(2)**, but also a positive effect on the heart muscle due to the decreased activity of isoenzymes LDH_2 with increasing concentration of these complexes in the control group.

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BS-CB P06

Solution study and cytotoxic activity of gold(III) complexes with L-histidine-containing peptides

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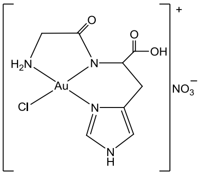
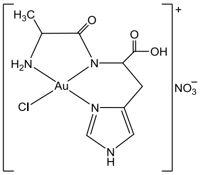
During the last decades, a great attention was devoted to synthesis and biological evaluation of gold(III) complexes as potential antitumor agents. The solution behaviour under physiologically relevant conditions of three gold(III) complexes with L-histidine-containing peptides, [Au(Gly-L-His-*N,N′,N′′*)Cl]$NO_3\cdot1.25H_2O$ [1] **(Au1)**, [Au(L-Ala-L-His-*N,N′,N′′*)Cl]$NO_3\cdot2.5H_2O$ [1] **(Au2)** and [Au(Gly-Gly-L-His-*N,N′,N′′,N′′′*)]$Cl\cdot H_2O$ [2] **(Au3)** has been investigated by application of ^1H NMR spectroscopy, UV-Vis spectrophotometry and cyclic voltammetry (CV). The obtained results showed that tridentate coordination of Gly-L-His and L-Ala-L-His dipeptides, as well as tetradentate coordination of Gly-Gly-L-His tripeptide stabilized +3 oxidation state of gold and prevented its reduction to Au(I) and Au(0). The cytotoxic activity of **Au1**, **Au2** and **Au3** was evaluated after 48 h by MTT assay toward five human tumor cell lines, namely MCF7 (human breast adenocarcinoma), HT-29 (human colon adenocarcinoma), HeLa (human cervix carcinoma), HL-60 (human promyelocytic leukemia), Raji (human Burkitt lymphoma) and one human normal cell line MRC-5 (human foetal lung fibroblasts). **Au1** was found to be active against all human malignant cell lines, while **Au2** and **Au3** showed different cytotoxic activity regading the type of cell line. Haematopoitec cells lines, HL-60 and Raji, were sensitive to **Au1** and **Au3** complexes, while HeLa cells were highly sensitive to **Au3** complex (IC_{50} = 0.0045 ± 0.0002 μM) and moderately sensitive to **Au1** and **Au2**. Neither of gold(III)-peptide complex was cytotoxic against human normal cell line, MRC-5.


Au1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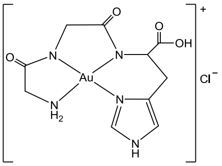
Au3

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BS-CB P07

Hydrolysis of the amide bond in *N*-acetylated L-methionylglycine in the presence of different binuclear $\{[Pt(L)(H_2O)]_2(\mu\text{-pz})\}^{4+}$-type complexes

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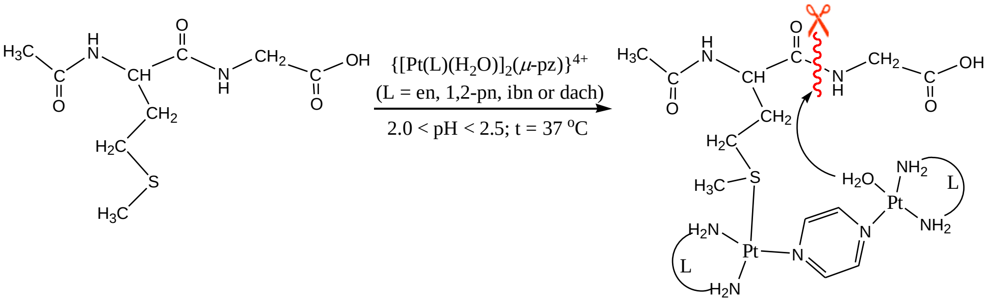
Recent studies in one of our laboratories [1] showed that binuclear $\{[Pt(en)(H_2O)]_2(\mu\text{-pz})\}^{4+}$ complex could be good reagent for amide bond hydrolysis in reactions with methionine-containing peptides (en is bidentate coordinated ethylenediamine and pz is bridging pyrazine ligand). In continuation of our previous investigations [1], in the present study the hydrolytic reactions of *N*-acetylated L-methionylglycine (Ac-L-Met–Gly) with different binuclear $\{[Pt(L)(H_2O)]_2(\mu\text{-pz})\}^{4+}$-type complexes, in which (L) is bidentate coordinated ethylenediamine (en), 1,2-propylenediamine (1,2-pn), isobutylenediamine (ibn) or 1,2-diaminocyclohexane (dach), were studied by ^1H NMR spectroscopy. All reactions were performed with equimolar amounts of the platinum(II) complex and peptide in the pH range 2.0 – 2.5 in D_2O as solvent and at 37 °C. In all investigated reactions, under above mentioned experimental conditions of the pH and temperature, hydrolysis of the amide bond involving the carboxylic group of methionine was observed. From the present results it can be concluded that the rate of the cleavage of this amide bond decreases as the steric bulk of bidentate coordinated diamine ligand (L) increases (en > 1,2-pn > ibn > dach). Our latest results together with those previously described [1] should be taken into consideration when designing new new polynuclear platinum(II) complexes as effective agents in the hydrolysis of methionine-containing peptides.



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BS-CB P08

In vitro trials of *Thymus glabrescens* essential oil and its main constituents with tetracycline

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Despite the development of synthetic antibiotics, infectious diseases retain a prominent position as a major worldwide cause of morbidity. Antimicrobial resistance is a major obstacle to the treatment of infectious diseases. Thus, a search for new and more sustainable antibiotics is a necessity. Many studies have shown significant antibacterial activity of essential oils against a wide range of resistant microbial strains [1]. Antibacterial activity of essential oils could be reflecting all the molecules present or only those present in high amounts. For the same reasons, no particular bacterial resistance or adaptation to essential oils has been described and secondary effects have not been confirmed. To enhance the efficacy of antimicrobial drugs, their combined use with essential oils is one of the promising strategies [2]. The present study was aimed to examine the chemical composition and antibacterial activity of *Thymus glabrescens* (thyme) essential oil, as well as the interactions of the thyme oil and its main constituents, in combination with tetracycline, in order to search for new, safe and efficacious antibacterial agents. Quantitative and qualitative data of the essential oil were obtained by gas chromatography (GC) and gas chromatography/mass spectrometry (GC-MS) analyses. Oxygenated monoterpenes were the most abundant compound class in the oil (57.30 %), with a geraniol (22.33 %) as the major compound. The group of phenolic monoterpenes (14.00 %) was dominated by thymol (13.79 %). The activity of the essential oil, geraniol and thymol was tested towards thirteen different bacteria. A broth microdilution method was used to determine the minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC). The interactions of the essential oil, geraniol, thymol and tetracycline toward five selected strains were evaluated using the microdilution checkerboard assay in combination with chemometric methods: principal components analysis (PCA) and hierarchical cluster analysis (HCA). The essential oil exhibited antibacterial activity against all tested bacterial strains *in vitro*, but the activities were lower than those of the standard antibiotic. A combination *T. glabrescens* oil and tetracycline produced predominantly synergistic and additive interactions (FIC indices in the range 0.21–1.10). These combinations reduced the minimum effective dose of the antibiotic and, consequently, minimized its adverse side effects. The synergistic interactions between thymol and tetracycline were more pronounced compared to essential oil-tetracycline or geraniol-tetracycline interactions.

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BS-CB P09

Chemical composition and antimicrobial activity of *Hypericum maculatum* Crantz essential oil

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The genus *Hypericum* L. (Guttiferae/Clusiaceae/Hypericaceae) includes more than 480 species that are naturally occurring on, or which have been introduced to, every continent in the world, except Antarctica [1]. Plants of the genus *Hypericum* have traditionally been used as highly esteemed medicinal plants. The aim of this study was to perform a detailed compositional analysis of the essential oil isolated from *H. maculatum* and to evaluate its antimicrobial potential.

The essential oil of fresh aerial parts of *H. maculatum* obtained by hydrodistillation was analyzed by GC and GC/MS. One hundred and nine compounds identified in *H. maculatum* essential oil, accounted for 97.8 % of the total oil. Germacrene D (21.5 %), nonane (6.5 %), (*E*)-β-farnesene (5.3 %), δ-cadinene (4.5 %) and ledol (4.4 %) were the most abundant components. Dominant class of compounds - terpenoids (86.9 %), was unevenly distributed between mono- and sesquiterpenoids (12.9 % and 74.0 %, respectively). Antibacterial potential of the oil was determined by using a broth microdilution assay against two Gram-positive (*Bacillus subtilis* ATCC 6633 and *Staphylococcus aureus* ATCC 6538) and three Gram-negative bacteria (*Escherichia coli* ATCC 8739, *Pseudomonas aeruginosa* ATCC 9027 and *Salmonella abony* NCTC 6017). Antifungal activity was tested against *Aspergillus niger* ATCC 16404 and *Candida albicans* ATCC 10231. The essential oil showed antimicrobial activity against all tested microorganisms being the most effective against *S. aureus* and *P. aeruginosa* with minimum inhibitory concentration of 1.56 mg/ml and bactericidal concentration of 6.25 mg/ml (for both strains).

Our results showed that *H. maculatum* essential oil possesses antimicrobial potential which may justify the usage of *Hypericum* species in traditional medicine.

Acknowledgments: *This work was funded by the Ministry of Education and Science of Serbia (Projects 172044 and 172047).*

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BS-CB P10

Isolation and purification of hypericin from *Hypericum Perforatum* L. extracts using a combined method: liquid-liquid extraction and HPLC

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St. John's wort (*Hypericum perforatum* L.) (SJW) is a widely distributed perennial herbaceous plant (Fig. 1.), well-known since ancient times as a medicinal herb with pharmacological properties such as antidepressant, antiviral, anti-inflammatory and antibacterial effects [1].

Hypericin, first isolated from *Hypericum perforatum* L., is a potent photosensitizer with strong pharmaceutical activities [2], with the following chemical structure, published in 1950 [3] (Fig.2.).

Fig.1. Hypericum Perforatum L.

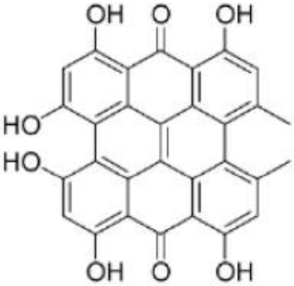

Fig.2. Chemical structure of hypericin

Therefore in the present work a procedure for hypericin extraction and purification using liquid-liquid extraction followed by high-performance liquid chromatography (HPLC) separation with photodiode array detection is presented.

Optimization of the procedure was carried out by changing the solvent (hexane, ethyl acetate, diethyl ether and water), the molar ratio and the amount of crude extract. After extraction and purification by HPLC the content of hypericin in the final extract was over 98 %.

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BS-CB P11

Methyl orange degradation and VX detoxication of nano-TiO_2 treated standard military textile

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The world-wide use of pesticides together with the possibility of chemical warfare agent's usage in military actions, terrorist attacks or in accidents, increased the risks of chemical contamination and consequently stipulated the need for the development of new protective materials and equipment with improved properties. Today, research are directed toward design of the so-called "smart textiles", which are capable of "self-decontamination", *i.e*. decomposition of toxic chemicals. We investigated two methods for the synthesis of TiO_2 nanoparticles, and their deposition on the standard military textiles (cotton/polyester 50%). Photocatalytic activity of the treated textiles was tested by degradation of organic dye, methyl orange (MeO), and chemical warfare agent *O*-ethyl *S*-(2-diisopropylamino)ethyl methylphosphonothiolate (VX). The second method, hydrolysis of titanium-tetraisopropoxide (TIP) in acidified water, proved to be superior comparing to the first method, which was performed in isopropanol, in the presence of the small amounts of water and triethylamine as the stabilizer of the obtained sol. Textile samples, treated with sol obtained from the second method, showed far better photocatalytic properties then samples treated with the sol obtained by the first synthetic procedure. We suppose that in the first synthesis formation of TiO_2 nanocrystals was not completed, nor was it upon subsequent treatment of the textile samples at 95 °C. One of the textile samples was tested for VX detoxication. Detection of VX by enzymatic AChE method, allowed us to monitor residual toxicity of the solution. Photocatalytic potency of the sample toward VX degradation was much lower than in MeO degradation testing. Although this result could be mainly attributed to the initial reaction conditions related to the low VX concentration, it is likely that better degradation efficiency could be also achieved through the optimization of the other reaction parameters for TiO_2 nanoparticles synthesis. We also performed evaluation of mechanical properties, tearing strenght, tensile strenght and air permeability of the textile samples.

Acknowledgements: *This work was supported by Serbian Ministry of Education, Science, and Technolgical Development, grant TR34034.*

BS-CB P12

Antiproliferative 4-aryl-4-oxo-2-*N*-cycloalkyl(aryl)idenebutanoic acids. Preparation, selectivity and 3D-QSAR study

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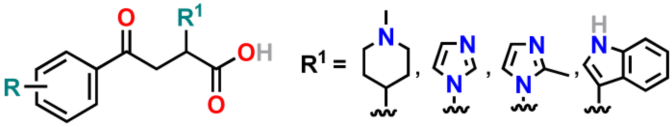
In this comunication we describe preparation, antiproliferative activity and selectivity of (*R*,*S*)-4-aryl-4-oxo-2-*N*-cycloalkyl(aryl)idenebutanoic acids (Scheme 1). Similar compounds having some biological activity are rare in literature, as well as in databases.



Scheme 1. *Structures of 4-aryl-4-oxo-2-N-cycloalkyl(aryl)idenebutanoic acids.* ***R****- = 4-F, 4-Et, 4-i-Pr, 4-t-Bu, 2,4-di-Me, 2,5-di-Me, 3,4-di-Me, 2,4-di-i-Pr, 2,4,6-tri-Et, tetrahydronaphtyl.*

Aroylacryliyc acids, precursors of title compounds, were prepared by Friedel-Crafts acylation of various substituted benzene with maleic anhydride. Target compounds were obtained by Michael addition of cyclic amines to aroylacryliyc acids. All compounds obtained were characterized by HR-MS, ^{1}H and ^{13}C NMR, and IR spectroscopy. Compounds exerted antiproliferative activity toward 5 human tumors cell lines (HeLa, LS174, K562, FemX and MDA-MB-361) in IC_{50} of 0.95-119 μM *in vitro,* as obtained by MTT test. Three compounds from the set showed cytotoxicity toward healthy human cells with IC_{50} values from 6.06-34.77 μM. Selectivity index of compounds span range from 7.5 to more than 40. Adducts having bulky hydrophobic substituents on the aroyl moiety showed better antiproliferative activity, compared to compounds bearing smaller substituents. Adducts obtained by *C*-addition of indole showed inferior activity. Two compounds (*N*-methylpiperazine derivates) have shown significant selectivity (healthy *vs*. tumor cells). Fluorescent staining of cells (acridine-orange /ethidium-bromide) has shown that tested compounds cause apoptosis of HeLa cells. 3D-QSAR (quantitative structure-activity relationship) models, based on GRIND-2 descriptors, derived from molecular interaction fields, obtained with 3 latent variables by Partial Least Square analysis, showed good statistics. Models showed that the activity trend of tested compounds were practically the same irrespective of human tumors cell lines tested; which prompts us to suppose that the mechanism of action of compounds is probably similar.

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BS-CB P13

Synergistic activity of *Satureja kitaibelii* essential oil and conventional antibiotics against some pathogenic bacteria

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The genus *Satureja* includes species that have been used in traditional medicine for the treatment of different conditions. So far, spasmolitic, analgesic, anti-HIV, antibacterial, antiviral, antioxidant and cytotoxic activities have been reported from several species of this genus. Many studies have shown significant antibacterial activity of essential oils against a wide range of resistant microbial strains [1,2]. Essential oils of *Satureja* species are also well known for their antifungal and antibacterial therapeutic values. The present study was aimed to examine the chemical composition and antibacterial activity of *Satureja kitaibelii* Wierzb. ex Heuff. (Lamiaceae) essential oil. In the search for new, safe and efficacious antibacterial agents, an in-depth evaluation of the *S. kitaibelii* oil–antibiotic mixture was followed. Gas chromatography (GC) and gas chromatography/mass spectrometry (GC-MS) were used to analyze the chemical composition of the oil. The antibacterial activity of the oil was investigated by the broth microdilution method against five bacterial strains. The interactions of the essential oil and three standard antibiotics: tetracycline, streptomycin and chloramphenicol toward selected strains were evaluated using the microdilution checkerboard assay in combination with chemometric methods. Oxygenated monoterpenes were the most abundant compound class in the oil (59.76 %), with geraniol (50.43%) as the major compound. The essential oil exhibited antibacterial activity against all tested bacterial strains *in vitro*, but the activities were lower than those of the standard antibiotics. The association of *S. kitaibelii* essential oil and standard antibiotics produced predominantly synergistic interactions (FIC indices in the range 0.21–0.87) against selected bacterial strains, especially Gram-negative bacteria, the pharmacological treatment of which is very difficult nowadays. These combinations reduced the minimum effective dose of the antibiotics and, consequently, minimized their adverse side effects [3].

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BS-CB P14

Essential oils composition of *Angelica pancicii* and *Angelica sylvestris*: a contribution to chemotaxonomic distinction

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The genus *Angelica* (Apiaceae) consists of about 60 species of ornamental, biennial or perennial herbs, which are distributed widely in Asia, Europe, and North America [1]. The species of genus Angelica are valuable medicinal plants [2]. According to some botanical classifications A. pancicii and A. sylvestris are considered as different species [2], but as synonyms for the same species to the others [3].

Herein we report identification of constituents from *A. pancicii* and *A. sylvestris* aerial parts essential oils. Essential oils obtained from dry aerial plant parts, harvested in the same vegetation phase from the same location, were analyzed by GC-MS. Yield of the *A. pancicii* and *A. sylvestris* essential oils were 0.14 % and 0.05 %, respectively. Total of 32 components were identified in essential oil from *A. pancicii* and 31 components from *A. sylvestris*. Identified components represent 96.07 % (*A. pancicii*) and 97.28 % (*A. sylvestris*) of the oil. The main compounds in *A. pancicii* essential oil were *β*-phellandrene (50.75 %) and *α*-pinene (13.59 %). Other more common components from *A. pancicii* were *α*-phellandrene (4.31 %), *δ*-3-carene (4.22 %), myrcene (3.75 %) and acorenol B (3.36 %). The major compounds of *A. sylvestris* were limonene (75.34 %) and *α*-pinene (9.55 %). *Ortho*-cymene, camphor, sabinene, myrcene and limonene-*cis*-oxide in *A. sylvestris* are represented in almost the same quantities (1.37 %, 1.24 %, 1.19 %, 1.18 % and 1.15 %, respectively).

Data on chemical composition of two studied essential oils, regarding both major and minor components, support classification of these two plants as different species.

Acknowledgments: *This work was funded by the Ministry of Education and Science of Serbia (Project 172047).*

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BS-CB P15

New complexes compounds of copper (II) and zinc (II) with the Schiff base N-(p-N,N-dimethylbenzylidene)-p-aminosalicylic acid – synthesis, characterization and biological activity

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This paper presents the synthesis, the characterization and the biological activity of the new complexes of Cu(II) and Zn(II) with the new Schiff base N-(p-N,N-dimethyl-benzylidene)-p-aminosalicylic acid (HL), derived from p-dimethylamino-benzaldehyde and p-aminosalicylic acid.

These new compounds synthesized were characterized by elemental chemical analysis and various physico-chemical methods as IR, electronic spectra, as well as by molar conductivity and magnetic susceptibility measurements.

The correlation of the elemental analysis with the results of the physico-chemical determinations suggest that the complexes described in this paper are of the $[M(L)(OAc)(H_2O)_3]$ type, where M = Cu(II) and Zn(II) and L = $C_{16}H_{15}N_2O_3^-$.

From the IR spectra, it is concluded that HL Schiff base binds to the metal ions through two oxygen donor atoms of groups (-COOH) and (-OH) respectively, located in favourable positions (-orto), of p-aminosalicylic acid moiety [1].

The electronic spectrum for the Cu(II) complex indicate a distorted octahedral structure of this complex.

The magnetic data confirm the stereochemistry proposed for this coordination compound. The Zn(II) complex is diamagnetic as expected for the d^{10} configuration [2].

The molar conductance values of the complexes suggest that no anions are present outside the coordination spheres.

The new compounds were screened for their antimicrobial activity towards seven microbial strains. Our results confirm that the antimicrobial activity increased by complexation [3] and also indicate that the $[Zn(L)(OAc)(H_2O)_3]$ complex was the most active one of the studied compounds.

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BS-CB P16

A spectroscopic and electrochemical investigation of the reactions of gold(III)-peptide complexes with glutathione under physiologically relevant conditions

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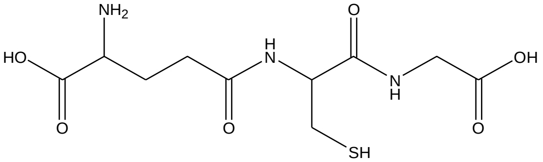
The possible involvement of gold(III) complexes in cancer treatment initiated an interest in the area of the interactions of Au(III) with different bioligands, such as peptides and proteins [1]. The course of the reactions of [Au(Gly-L-His-*N,N′,N′′*)Cl]NO_3·1.25H_2O, [Au(L-Ala-L-His-*N,N′,N′′*)Cl]NO_3·2.5H_2O and [Au(Gly-Gly-L-His-*N,N′,N′′,N′′′*)]Cl·H_2O complexes with tripeptide glutathione (GSH; γ-L-Glu-L-Cys-Gly) has been studied by application of ^{1}H NMR spectroscopy, UV-Vis spectrophotometry and cyclic voltammetry. All reactions were performed under physiologically relevant conditions in 50 mM phosphate buffer, containing 4 mM NaCl at pH 7.40 and 37 ^{o}C. In the reactions of [Au(Gly-L-His-*N,N′,N′′*)Cl]NO_3·1.25H_2O and [Au(L-Ala-L-His-*N,N′,N′′*)Cl]NO_3·2.5H_2O with glutathione, [Au(Gly-L-His-*N,N′,N′′*)(GS)] and [Au(L-Ala-L-His-*N,N′,N′′*)(GS)] complexes with monodentate coordinated tripeptide through the sulfur atom of the cysteine residue were formed. The obtained complexes were stable during 48 h, and no formation of Au(I) species or metallic Au(0) was observed, confirming that gold remains in +3 oxidation state in both reactions. However, no coordination of the thiolate sulfur atom of glutathione to [Au(Gly-Gly-L-His-*N,N′,N′′,N′′′*)]Cl·H_2O was occured. The [Au(Gly-Gly-L-His-*N,N′,N′′,N′′′*)]Cl·H_2O complex was stable in the presence of glutathione for 48 h at pH 7.40 and 37 ^{o}C. The obtained results are in contrast with previous findings for the reaction between GSH and $[Au(CN)_4]^-$ complex at pH 7.40 in phosphate buffered solution, that proceeds through the gold(III) complex reduction to $[Au(CN)_2]^-$, and GSH oxidation to glutathione disulfide ($GSSG^{2-}$) [2].



glutathione

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BS-CB P17

Enzymatic Protein Hydrolysates from the green microalga *Desmodesmus communis*

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Proteins are the most abundant component in the algal biomass, representing more than 40% of the total dry weight, whereas lipids can be found as 20 to 30% of the biomass depending on which strain is used. Therefore the production of large amounts of lipids from microalgae involves the production of a large deal of protein, which can in fact be expected to double the amount of lipids produced. So, it is clear that the protein production must be valorised to make the process economically positive. [1]

Extraction of added-value protein fractions from algal biomass for techno-functional applications in feeds, soil enhancers or as a source of nutrients for the cultivation of microalge in mixotrophic culture, can considerably increase the commercial value of microalgal biomass.[2]

This paper focuses on the development of a process for enzymatic hydrolysis of cell proteins in green microalga *Desmodesmus communis*. Enzymatic hydrolysis is selected instead chemical hydrolysis to produce a high quality product, rich in essential amino-acids, free of toxic degradation products because the process is carried out under mild conditions.

The influence of reaction parameters on hydrolysis of extracted biomass with different proteases such as Alcalase 2.5L, Flavorzyme 1000L and Savinase 8.0T was considered, both alone or as a cocktail of enzymes. Significant changes in the degree of hydrolysis (from 30% until more than 70%), were observed which varied by using up to 4% (w/w) units of enzyme on suspension of the treated algae (20%).

The process enlarges the portfolio of products that can be obtained from microalgal biomass and it is a new possibility to enhance the economic viability of microalgae-based biofuels production processes.

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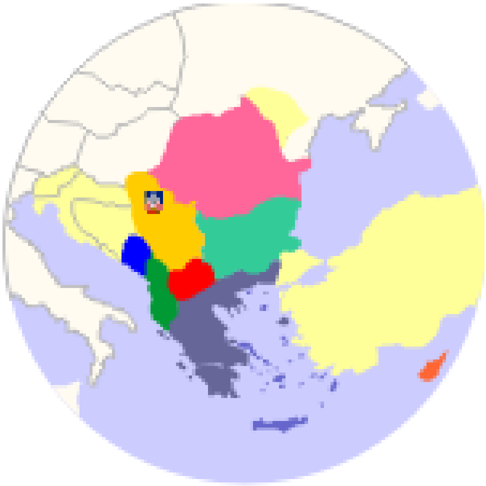

Computational Chemistry

O 11 BS-CC

Molecular modelling of 5HT$_{2A}$ receptor and key protein-ligand interactions

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We report molecular modelling of 5HT$_{2A}$ receptor and docking analysis of arylpiperazine common structure ligands [1-3]. In order to explain obtained experimental results, we used molecular modelling and docking analysis. Homology model of 5HT$_{2A}$ was based on crystal structure of β_2 adrenergic receptor (PDBID 3D4S) [4]. Obtained model was additionally energetically relaxed by explicit membrane molecular dynamics simulation. Ligands were docked as flexible while receptor was kept rigid.

Observed interactions were, beside the crucial salt bridge between conserved Asp 155 and protonated nitrogen atom of ligand, mainly aromatic (edge-to-face and CH-π interactions) and hydrogen bonds. Important amino acids residues for arylpiperazine ligand binding are: Asn 343, Tyr 370, Ser 159, Phe 339, Trp 336, Val 156, Phe 234, Val 366, Val 235 and Ile 152 (Fig. 1).

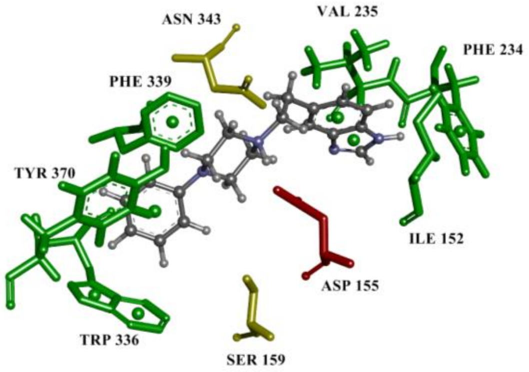

Figure 1. Docking results of 5HT$_{2A}$ receptor and 5-(2-(4-phenylpiperazin-1-yl)ethyl)-1H-benzimidazole ligand. Only key amino acid residues are shown for clarity.

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O 12 BS-CC

Systematic DFT study of adsorption of some non-metal atoms on defect-free MgO(100)

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Adsorption of non-metals on metal oxide surfaces, being important from catalytic point of view, was extensively investigated both experimentally and theoretically [1,2]. In order to comprehend the enhancement of catalytic activity upon functionalization with metallic catalytic components, as a first step, one should investigate the mechanism of oxide surface interaction with different reactive species [2]. Following this statement, in this contribution we present a systematic Density Functional Theory study of the adsorption of non-metal p-elements as well as Hydrogen, on stoichiometric MgO(100) surface. The adsorption of Hydrogen, Carbon, Nitrogen, Oxygen, Fluorine, Sulfur, Chlorine and Bromine atoms on a defect-free MgO(100) surface was investigated, and the adsorption trends were established. Comparing the adsorption energies of specified atomic adsorbates, we concluded that the sites involving oxygen centers were preferential ones, while the sites involving Mg surface centers were energetically unfavorable or unstable. Among investigated adsorbates the strongest interaction with MgO(100) surface was evidenced in the case of Carbon, with the adsorption energy of -2.62 eV, while Fluorine, Oxygen and Sulfur adsorbed with mutually similar energy amounting approximately -2 eV. Adsorption energy of hydrogen atoms was found to amount to only -0.56 eV *per* atom. By a cross-examination of electronic structure of adsorbed atoms and their adsorption energies determined by different methodologies, we concluded that spin polarization effects should be accounted for in order to describe properly the adsorption process, especially if one deals with the atomic adsorbates with more than one unpaired electron.

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O 13 BS-CC

Docking studies of 3-hydroxy-3-arylpropionic acids as potentially selective COX-2 inhibitors

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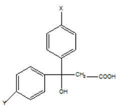
Although non-steroidal anti-inflammatory agents (NSAID) are numerous, broad used and can be procured as OTC drugs, search for new non-steroidal NSAID is continuing. Main motive is to find compound which selectively inhibits inducible form of enzyme cyclooxygenase (COX-2), but would have at least 10 times less effect on constitutive form (COX-1). If this selectivity concept is achieved, adverse effect on gastric mucosa would be avoided [1]. According to current docking studies, a compound is considered selective if it can maintain interactions in hydrophilic side pocket, so called P3 region in the active site of COX-2 [2]. The aim of this study was to determine the impact of substitution of one or both phenyl rings in 3-hydroxy-3,3-diphenylpropanoic acid with some simple substituents on selectivity towards COX-2 inhibition. Molecular docking calculations were performed using Autodock v4.0.1 into the 3D structure of the catalytic site of COX-2 enzyme (pdb code: 1cx2). Structure of each compound was generated using the ChemOffice v7.0 Ultra software package and have been MM2 optimized. Each docking experiment consisted of 100 docking runs with 150 individuals and 500,000 energy evaluations. The structures were incorporated into 40x40x40 grid points receptor pocket, which was centered to the position of ibuprofen in crystallographic structure of the complex. Ibuprofen was used as a reference compound because of its structure similarity to tested compounds. All of the compounds have lower binding energies than ibuprofen (Fig. 1) and all of these compounds have the right structure which enables penetration into P3 region in the COX-2. Compound containing dimethylamino group penetrates deepest into this region indicating the best selectivity ratio of all tested compounds.

X	Y	E of R enatiomer (kcal/mol)	E of S enantiomer (kcal/mol)	
NO_2	/	-7,67	-7,58	 3-hydroxy-3,3-diphenylpropanoic acid
CF_3	/	-7,27	-6,92	
Cl	/	-7,45	-7,30	
CH_3	/	-7,41	-7,29	
$NH(CH_3)_2$	$NH(CH_3)_2$	-8,86		
OCH_3	OCH_3	-7,33		
Cl	Cl	-7,68		

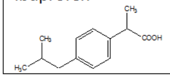
Ibuprofen	E of R enantiomer (kcal/mol)	E of S enantiomer (kcal/mol)
	-6,90	-7,44

Fig. 1. Binding energies of acid derivatives compared to binding energy of ibuprofen

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O 14 BS-CC

Photoactivation mechanism of DNA photolyase

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Changes and damages in the DNA structure, such as, excision or modification of bases or alternation of sugar-phosphate groups are often caused by UV light, ionizing radiation, toxic substances and environmental pollution. To maintain genetic stability, cells protect themselves against these kinds of damages. Moreover, the main DNA repair processes in prokaryotic and eukaryotic cells are quite similar.

The DNA photolyases repair the most common type of the DNA defects – cyclobutane pyrimidine dimers (CPD) and (6-4)-photoproducts. The enzyme contains two photoactive cofactors, folic acic and FADH$^-$, which both can get in the excited state [1]. Folate cofactor plays a role of a photon antenna molecule, which harvests and transfers the excitation energy to the catalytically active FADH$^-$ form. The electron transfer from the excited FADH$*^-$ state to the pyrimidine dimer causes a splitting of the cyclobutane ring and back electron transfer to FADH$^\bullet$. Thus, photolyase repairs UV (200-300 nm) induced damage in DNA by splitting the ring of the CPD dimer into pyrimidine monomers [2, 3].

This presentation is on the theoretical computational study of the DNA photolyase from *E. coli*. Continuum electrostatic method [4] is employed to get a full insight into the photoactivation mechanism of the enzyme. Protonation state of titratable residues, the redox potentials of tryptophan triad, energetics and the reaction rates are calculated and compared with available experimental data. The free energies of all potentially relevant states for the radical transfer during the photoactivation process are evaluated.

Besides a general introduction to the photoactivation and photorepair mechanism, and the structure-function interrelation in the DNA photolyase, this presentation will also address a several long-time controversial questions, such as: Why is photolyase one of very few FAD containing proteins which resting (ground) state is a radical state FADH$^\bullet$? What is the distance between the CPD dimer and redox-active cofactor in the CPD–protein complex? Why does FADH cofactor adopt a quite unusual U-shape and what is the functional purpose of having such a form? Hopping vs. super-exchange mechanism of the ET pathway in the photoactivation process of FADH chromophore?

The obtained results are in very good agreement with the experiments [3, 5] and may be relevant for all other types of photolyases and cryptochromes, since they have a high degree of the sequence similarity including the conserved tryptophan triad present in all of these structures [6].

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O 32 BS-CC

Energetics of the steps in proton pumping mechanism and preventing of backflow reactions in cytochrome *c* oxidase

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Cytochrome *c* oxidase (CcO) is the terminal enzyme of aerobic respiration, which is responsible for processing most of the biological oxygen and generating electrochemical proton gradient in aerobic cells [1]. The energy released from the reduction of molecular oxygen to water is used to pump protons across the mitochondrial or bacterial membrane. The structure of the enzyme has been solved for several organisms; however details of its molecular mechanism of proton pumping still remain elusive.

Recent time-resolved optical and electrometric experiments on the O→E transition have suggested a sequence of reaction steps for the proton-translocation mechanism of CcO [2]. The pump function introduces a mechanistic requirement of a valve that prevents protons from flowing backwards during the process. It was recently found that Glu242, a key amino acid in transferring protons to be pumped across the membrane and to the site of oxygen reduction, fulfills the function of such a valve by preventing simultaneous contact to the pump site and to the proton-conducting D-channel [3, 4]. Here we have included the conformational gating by Glu242 into the framework of the proposed His291 pumping model [5]. DFT/electrostatic calculations are employed to obtain energetics of proton and electron transfer reaction steps during the O→E transition, while transition state theory is used for estimating activation energies and kinetic barriers from the rate constant of transitions. The energy profile of the reaction mechanism is studied by exploring how the redox state of the adjacent metal centers, dielectric effects, and membrane potential gradient, affect the energy levels and the leaks of the Glu-valve.

Special emphasis is made on side-reactions that may short-circuit the pump, and the means by which these may be avoided. The state with the proton on the pump site (His291) is especially vulnerable to leak back to Glu^{-} instead of being released to the *P*-side of the membrane, what would result in a loss of proton-pumping.

Obviously, there are more different control mechanisms and gating situations employed by the enzyme to ensure the unidirectionality of the proton translocation and to prevent proton leak in the opposite direction.

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BS-CC P01

Clustering of epitopes in ordered and disordered protein regions: Lessons from the EBV nuclear antigen EBNA 1

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T-cell epitope prediction, based on major histocompatibility complex (MHC)-binding peptide affinities, is considered as a valuable step in vaccine design, yet further investigations are nedeed to provide explanations to selective epitope processing and immunodominance. Disordered protein regions are prevalently hydrophilic, extremely sensitive to proteolysis *in vitro*, and were found to have low number of T-cell epitopes in nuclear systemic autoantigens [1]. According to NetMHCpan-2.0 and NetMHCIIpan-1.0 T-cell epitope-predictor servers [2, 3], and 10 disorder predictors [4], used in this study, frequencies of epitopes from 619 proteins, predicted to bind 1469 human leukocyte antigen (HLA) class-I and 517 class-II alleles with unique pseudosequences, were found to be 1.01 to 24.74 times higher (depending on disordered predictor) in ordered than in disordered regions. Epitopes located in ordered protein regions were prevalently hydrophobic. Discovered relations were also valid if proteins were grouped according to main taxonomic categories, or if alleles were grouped according to HLA-I and HLA-II supertypes (except for supertype A3 in which the main part of recognized epitopes was prevalently hydrophilic). Epstein-Barr virus (EBV)-associated malignancies can be distinguished by the paterns of latent viral gene expression. EBV nuclear antigen 1 (EBNA 1) is expressed in latency states of EBV-associated cancers and is also associated with autoimmune diseases [5]. Majority of predicted and experimentally found HLA-I and HLA-II epitopes are located in the functionally important C-terminal region of EBNA 1, which overlaps the consensus of ordered regions of all analysed disorder predictors, and in the putative disordered-binding structures, predicted by ANCHOR predictor [4]. B-cell epitopes: PPPGRRP (residues 398-404) and GGSGSGPRHRDGVRR, (residues 58-72), from EBNA 1, associated with early events of lupus autoimmunity [5], were predicted to correlate with disorder-binding structures (predicted by ANCHOR) and vicinity of the protein regions with elevated crystalographic B factor (predicted by DisEMBL-hot loops).

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BS-CC P02

An *ab initio* study of antimony dicarbide (C_2Sb)

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The earlier theoretical studies of dicarbides C_2P [1] and C_2As [2,3] strongly supported the analysis of experimental data by the Clouthier' group [4,5]. The subject of the present study is a dicarbide of the next element in XV group - C_2Sb. Antimony dicarbide was investigated employing single-reference coupled cluster [RCCSD(T)] and multi-reference configuration interaction [MRCI(Q)] methods. The correlation consistent basis sets were used: aug-cc-pVTZ basis set for C, and aug-cc-pVTZ-PP with pseudopotential, which takes into account relativistic effects for Sb. Additionaly, corrections due to all-electron correlations [(+core corr.)RCCSD(T)], core-valence correlation [using cc-pwCVTZ(-PP) basis for C(Sb)], and spin–orbit effects were also included. All calculation were realized using Molpro 2010.1 program package [6].

The potential energy surface is extremely flat and the minimum of ground state was found to be the bent-structure ($1^2A''$) with C-C-Sb angle of 156.7 degree [our best single-referece result obtained by the (+core corr.)RCCSD(T)/cc-pwCVTZ(-PP)]. The linear structure ($X^2\Pi$) was found to be a transition state (imaginary frequency of 27 cm^{-1} for bending mode), only 0.07 kJ mol^{-1} higher in energy than the bent structure. T-shaped cyclic C_{2v} ($^2B_2$) geometry was found about 2.9 kJ mol^{-1} higher in energy than the global minimum. The linear CSbC is about 470 kJ mol^{-1} less stable than the linear CCSb. Owing to very small barrier to linearity, which is about 200 times smaller than the zero-point correction, and the high amplitude bending mode with low frequency (43 cm^{-1}), it was concluded that C_2Sb is quasi-linear and the linear $X^2\Pi$ species should be detected in experiments as its ground state.

The molecular orbital analysis was performed. The spin–orbit constant for the ground state was predicted to be 1805 cm^{-1}. The calculated dissociation energies of C_2Sb ($X\ ^2\Pi$) are relatively high, 355.7 kJ mol^{-1} and 603.6 kJ mol^{-1}, for losing two and one carbon atom, respectively. The low-lying excited valence-type electronic states were investigated at relaxed linear nuclear arrangments. The transitions from the ground state to the $1^2\Delta$, $1^2\Sigma^-$, $2^2\Pi$, and $1^2\Sigma^+$ state should be sufficiently intense to be observed. The most probable transition was found to be $X^2\Pi$-$1^2\Delta$, with the origin of electronic spectrum at approximately 11900 cm^{-1}.

We hope that the predicted geometry and electronic structure, as well as electronic spectra, will be of importance for future experimental and theoretical investigation of antimony dicarbide, which has not been detected thus far.

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BS-CC P03

Geometries and stability of neutral and cationic hyperlithiated clusters - $Li_nI^{(0,+1)}$ (n=1-6)

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The subject of the present study is non-stoichiometric heterogeneous lithium clusters with iodine - $Li_nI^{(0,+1)}$ (n=1-6). We present the lowest energy isomers of the neutral and cationic lithium-iodide clusters up to six Li atoms and discuss changes in their geometry structure and binding energy per atom (as one of the most important parameter of stability) with cluster growing. These clusters were experimentally mainly examined through mass spectrometry and ionization energy measurements [1,2].

The lowest energy isomers were found by the random kick procedure [3]. Obtained geometries were refined using B3LYP functional in the augmented correlation-consistent triple-zeta basis sets for Li (aug-cc-pVTZ) and corresponding triple-zeta basis with small-core relativistic pseudopotential for I (aug-cc-pVTZ-PP). In order to calculate precise binding energies, single-point calculations were performed for B3LYP-optimized geometries. These energies were obtained using couple cluster singles and doubles with perturbative inclusion of triples and correlation of all electrons [ccRCCSD(T)] in core-valence correlation consistent basis sets [cc-pwCVTZ(-PP)].

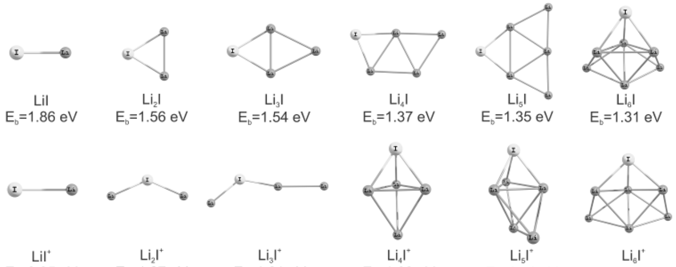

Figure 1. Optimized structures of $Li_nI^{(0,+1)}$ (n=1-6) with corresponding binding energies per atom.

From Figure 1 it can be seen that the lowest energy isomers of the neutral species, up to five Li atoms, are planar structures. On the other hand, for cationic species, turning point from planar to the compact three dimensional structures is three Li atoms. Considering binding energies per atom of the neutral species, we can see a general trend of decreasing stability with cluster growing. However, it should be noted the increase of stability of clusters with an even number of electrons (LiI, Li_3I and Li_5). This is even more pronounced for cationic species; therefore Li_2I^+ and Li_4I^+ are the most stable charged clusters.

We hope that these results will be of importance for further systematic investigations of those or similar clusters.

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BS-CC P04

Toxicological and receptor-based 3-D QSAR studies of *in vivo* anticoagulant activity of novel 3-(1-aminoethylidene)chroman-2,4-diones and 4-hydroxy-3-(1-iminoethyl)-*2H*-chromen-2-ones

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Eight novel 3-(1-aminoethylidene)chroman-2,4-diones and 4-hydroxy-3-(1-iminoethyl)-*2H*-chromen-2-ones, synthesized by conventional and microwave-assisted procedure, respectively, were evaluated as *in vivo* anticoagulants by *intraperitoneal* application to adult male Wistar rats. Two of them, **2f** and **2a**, in concentration of 2 mg/kg of body weight, presented remarkable activity (PT = 130 sec; PT = 90 sec) upon seven days continuous application [1]. Active compounds were proven to be non-toxic according to results of rat serum screening, histopathological and DNA damage studies. The catalytic activities of AST, ALT and ALP, and concentration of bilirubin were slightly increased in comparison with saline as negative control, and lower or comparable with warfarin as the positive one. The histopathological examination showed no significant hepatocyte damage. In addition no visual DNA damage was perceived by comet assay. The activity of compounds was further regarded on molecular level. Since coumarin based anticoagulants are competitive inhibitors of vitamin K-2,3-epoxide reductase subunit 1 (VKORC1), molecular docking studies were performed to position compounds into the active site of VKORC1 [2]. The conformational analysis pointed out amino acid Cys135 as a catalytic one [3]. Since the nature of interaction is hydrogen bond, SH group hydrogen atom is transferred towards C-4 carbonyl group of **2f** (d_{HB} = 2.688 Å) and **2a** (d_{HB} = 2.913 Å). The alignment of **2f** and **2a** is conditioned by hydrophobic interactions between the chroman-2,4-dione core and Tyr139. Receptor-based 3-D QSAR studies (CoMFA, $r^2 = 0.927$, $q^2 = 0.793$; CoMSIA steric $r^2 = 0.908$, $q^2 = 0.785$; CoMSIA hydrophobic, $r^2 = 0.929$, $q^2 = 0.724$; CoMSIA hydrogen donor and acceptor, $r^2 = 0.853$, $q^2 = 0.764$) revealed favorable pharmacophoric regions which provide anticoagulant activity. Steric interactions with Tyr139 were confirmed *via* CoMFA and CoMSIA green contorurs, along with grey CoMSIA hydrophobic maps, while hydrogen acceptor potential of 4-carbonyl group was seen by red CoMFA electrostatic fields and light blue CoMSIA hydrogen acceptor polyhedron.

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, Grants No. III43004 and III41010

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BS-CC P05

Solvatochromic and quantum chemical studies on the structures of some arylazo pyridone dyes

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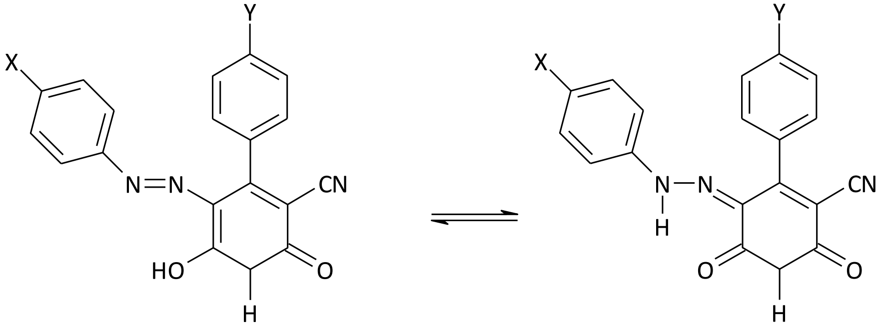
A series of some arylazo pyridone dyes (Figure 1) was synthesized from the corresponding diazonium salt and 6-hydroxy-4-aryl-3-cyano-2-pyridone using classical reaction for the synthesis of the azo compounds [1]. The structure of the dyes was confirmed by UV/Vis, FT-IR, ^{1}HNMR and ^{13}CNMR spectroscopic techniques and elemental analysis. The solvatochromic behavior of the dyes was evaluated with respect to their visible absorption properties in various solvents. The azo-hydrazone tautomeric equilibration was found to depend on the substituents as well as on the solvent [2]. The obtained results show that arylazo dyes with nitro group in the benzene ring in position 4 of pyridone nucleus have stronger batochromic shifts than other two series of azo dyes in all used solvents. The geometry data of the investigated dyes were obtained using DFT quantum chemical calculations. The obtained calculational results are in very good agreement with the experimental data.



(X = H, OH, CH_3, Cl, Br, I, F, CN, $COCH_3$, NO_2)

(Y = H, OCH_3, NO_2)

Figure 1. Azo-hydrazone tautomerism of investigated arylazo pyridone dyes.

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BS-CC P06

Electronic structure of several lowest-energy isomers of dicyanoacetylene and its ions: a multireference study

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Electronic structure of the ground and low-lying excited valence electronic states were investigated for several most important isomers using CASSCF [1], CASPT2, [2] and MRCI [3] multi-reference methods in the aug-cc-pVTZ basis set [4] for the title species.

B3LYP-geometries were used for the subsequent electronic structure calculations. The active space could not be the full-valence space, due to large number of valence electrons [CAS(26,24)]. Therefore, CASSCF(12,12) was used for the neutral and the cation. For the active space only π orbitals were chosen (3 π_g and 3 π_u). The lowest singlet and triplet states for several neutral isomers, and doublet and quartet states for ions were calculated. Energies were refined using the CASPT2 and MRCI that take into account dynamic correlation of electrons. Standard convergence criteria were applied in all computations. Electronic structure computations were realized using MOLPRO 2012.1 [5,6] program package.

The dominant configurations for the lowest energy isomers of the neutral and the cation are: $\ldots 13\sigma_g^2 1\pi_u^4 1\pi_g^4 2\pi_u^4$ and $\ldots 13\sigma_g^2 1\pi_u^4 1\pi_g^4 2\pi_u^3$, respectively. On the contrary, the lowest-energy isomer of the anion species is not linear.

Natural molecular orbitals were obtained from the state-average complete active space SCF (SA-CASSCF) method. HOMO and LUMO orbitals were analyzed, and the valence orbitals for several isomers are shown using the MacMolPlt program [7]. Additionally, true electrostatic potential is shown for the several interesting isomers.

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BS-CC P07

Identification of key D2 receptor-ligand agonist/antagonist interaction

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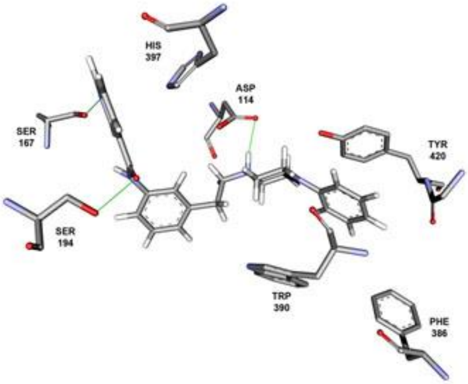
There are no crystal 3D structures available for human D2 receptor despite it's vital function and importance as therapeutic target [1]. Here we present, recent progress in molecular modeling of the dopamine D2 receptor [2], based on crystal structure of dopamine D3 receptor [3]. To determine key interactions responsible for agonist/antagonist activity, we used computer docking analysis together with experimental data. Total of 5 dopaminergic arylpiperazine like ligands were tested using cAMP direct immunoassay kit and obtained results correlated with ligand structures docked into proposed D2 receptor model.
Preliminary results show that for antagonist activity ligand has to partially occupy receptor bind site while interacting with ASP 116 and hydrophobic pocked formed by PHE 386, TRP 390 and TYR 420. Partial agonists have to fill in whole bind site and interact with at least one serine residue (SER 167, 194 or 197), while more interactions with amino acid residues located in second extracellular loop lead to stronger agonist activity.



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BS-CC P08

In silico ADME and QSAR studies of some benzimidazole derivatives to predict antifungal activity

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In this paper various derivatives of benzimidazole have been evaluated against yeast *Saccharomyces cerevisiae*. Quantitative structure-activity relationships (QSAR) attempts to find consistent relationships between the variations in the values of molecular properties and the biological activity for a series of compounds, so that these rules can be used to evaluate new chemical entities [1-4]. The correlations between minimum inhibitory concentration and some absorption, distribution, metabolism and excretion (ADME) parameters were investigated, and the mathematical models were developed for predicting the antibacterial activity of this class of compounds. The quality of the multiple linear regression (MLR) models was validated by the leave-one-out (LOO) technique, as well as by the calculation of the statistical parameters for the developed models and the results are discussed based on the statistical data. The high cross-validated r^2 values (r^2_{CV}) and low residual value indicate the predictive ability of the developed QSAR models. It could be concluded that new molecules should be designed by considering the plasma protein binding (PPB%) and human colon adenocarcinoma cell permeability (Caco-2) of benzimidazole molecule. The results of this study indicate that ADME parameters have a significant effect on the antibacterial activity of this class of compounds. Principal component analysis (PCA) and agglomerative hierarchical clustering algorithms (HCA) analysis have shown that investigated compounds can be classified according to their ADME parameters. This study can improve further molecular modeling and *in vivo* pharmacological research of benzimidazole derivatives.

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BS-CC P09

Ab initio calculations of aromatic protein-ligand interactions inside the binding site of dopamine D2 receptor

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In order to explain trends in experimental binding affinities of 1-{2-[5-(1H-benz-imidazole-2-thione)]ethyl}-4-arylpiperazines-type ligands to dopamine D2 receptor, we studied *ab initio* aromatic edge-to-face protein-ligand interactions in receptor binding site. Ligand structure was divided into head, linker, body and tail part. We focused to explain binding site interactions with tail part of the ligand (Fig 1.). In the binding site we identified three aminoacid residues, Tyr 420, Trp 390 and Phe 386, involved in edge-to-face interactions with ligand. In order to alter the exhaustiveness of calculations, but still keep all interactions of interest, our system was simplified. Aminoacid residues in the binding site Tyr 420, Trp 390 and Phe 386 were simplified to 4-methylphenol, 3-methyl-1H-indole and toluene, respectively (Fig 2.). Ligands were simplified to N,N-dimethyl-substituted anilines. Simplified structures were optimized using DFT B97D level of theory with TZV basis set. Optimal distance between aminoacid residues and ligand was obtained by scanning energies with distances between ring centroids from 4 to 8 Å on the same level of theory. Geometries were than reoptimized using cc-PVTZ basis set on the same DFT level and single point energies were calculated on distances obtained at previous lower level of theory. Binding energies were calculated from difference of three energies: energy of model system with ligand, without ligand and energy of ligand. Counterpoise error was implemented. The results obtained from our calculations show that trend in calculated binding energies follows experimental trend [1].

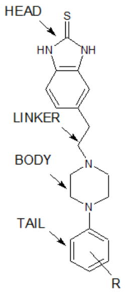

Figure 1. Ligand structure

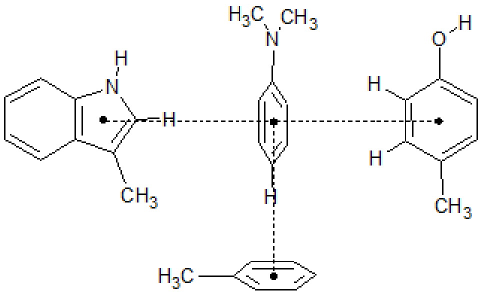

Figure 2. Simplified binding site of dopamine D2 receptor with ligand

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BS-CC P10

Experimental and theoretical study of substituent effect on ^{13}C NMR chemical shifts of 5-arylidene-2,4-thiazolidinediones

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The electronic structure of 5-arylidene-2,4-thiazolidinediones has been studied by using experimental and theoretical methodology. The theoretical calculations of the investigated 5-arylidene-2,4-thiazolidinediones have been performed by the use of quantum chemical methods. The computational studies include MP2 geometry optimization, DFT calculations of NMR chemical shifts and calculations of atomic charges with NBO method by the use of GIAO/WP04/cc-pVDZ method to calculate NMR chemical shifts and MP2/6-311G** method to calculate NBO atomic charges. The calculated ^{13}C NMR chemical shifts and NBO atomic charges provide an insight into the influence of such a structure on the transmission of electronic substituent effects. Linear free energy relationships (LFERs) have been further applied to their ^{13}C NMR chemical shifts. The correlation analyses for the substituent-induced chemical shifts (SCS) have been performed with σ using SSP (single substituent parameter), field (σ_F) and resonance (σ_R) parameters using DSP (dual substituent parameter), as well as the Yukawa–Tsuno model. The presented correlations account satisfactorily for the polar and resonance substituent effects operative at C_β, and C_7 carbons, while reverse substituent effect was found for C_α.

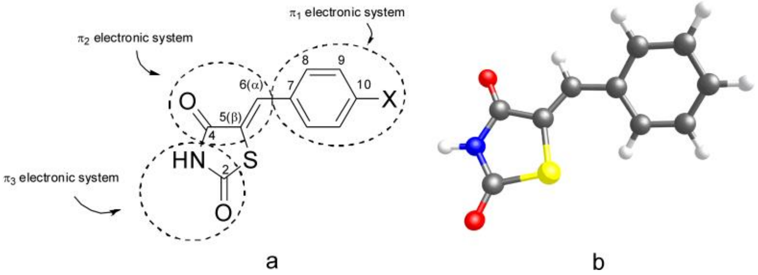

Fig. 1 *Chemical structure of 5-arylidene-2,4-thiazolidinediones, where X is: H; methyl (Me); isopropyl (iPr); methoxy (OMe); ethoxy (OEt); hydroxy (OH); amino (NH_2); dimethylamino (NMe_2); chloro (Cl); bromo (Br) and nitro (NO_2)*

BS-CC P11

Molecular docking provides understanding of the *in vivo* antigenotoxic activity of naturally occurring aromatic compounds: myricetin, quercetin, rutin, and rosmarinic acid against ethyl methanesulfonate

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Due to inconsistent results regarding the antimutagenicity of some phenolic compounds recorded in the literature, the antigenotoxic effects of four selected phenolic compounds, myricetin, quercetin, rutin, and rosmarinic acid, against DNA damage induced by alkylation with ethyl methanesulfonate (EMS) [1], were evaluated in *Drosophila melanogaster* males using the sex-linked recessive lethal (SLRL) test [2]. To understand the exceptional activity of all examined compounds, consideration of results was transpassed on molecular level, seeking for mechanisms of DNA protection. Thus, molecular docking studies enclosed diverse mechanisms of antigenotoxic behaviour of tested compounds. During the treatment, *D. melanogaster* males were exposed to a monofunctional alkylating agent EMS in concentration of 0.75 ppm, 24 h prior to one of the selected phenolic compounds in concentration of 0.1%. EMS induced considerable DNA damage as shown by significant increase in the frequency of germinative mutations. Mutations are reflected on DNA sequence by emergence of O^6-ethylguanine and O^4-ethylthimine, lesions which are carcinogenic and mutagenic and cause unnatural GT and TG transition mutations [3]. Upon post-treatments with all selected phenolic compounds the frequency of mutations decreased with high significance ($p < 0.001$***). This decrease, *i.e.* phenolic compounds induced protection of DNA against alkylation, is primarily dependent on reparation of lesions by O^6-alkylguanine-DNA alkyltransferase, enzyme which removes ethyl groups and restores target nucleotides in their native state. Therefore, since there is no available crystallography data to enclose the reparation of ethyl lesions, O^6-ethylguanine and O^4-ethylthimine were docked into the active site of O^6-alkylguanine-DNA alkyltransferase to confirm that particular lesions can be repaired [4]. Finally, myricetin and quercetin protected dealkylated nucleotides by forming the hydrogen bond *via* B ring hydroxyl group with O^6-guanine and O^4-thymine, while rutin and rosmarinic acid encircled nucleotides making an impermeable barrier for the EMS molecule [5].

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, Grants No. III43004 and III41010.

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BS-CC P12

Solvatochromic and quantum-chemical investigations of *N*-aryl-2-methyl-succinimides: substituent effect on intramolecular charge transfer

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A series of some *N*-aryl-2-methylsuccinimides (Figure 1) has been synthesized and their solvatochromic properties have been studied in a set of 15 solvents of different polarity. The effect of specific and non-specific solvent-solute interactions on the position of their absorption bands has been evaluated by using the solvent parameter sets of Kamlet and Taft. The interpretation of effect of different substituent patterns on the solvatochromic properties of the investigated compounds is based on quantum chemical calculations which have been performed by the density functional theory DFT/B3LYP method using 6 311G(d,p) basis set. The theoretical absorption frequencies show very good agreement with the experimental values. The energy gaps between the HOMO and LUMO orbitals have also been analyzed. It is demonstrated that different substituents change the conjugation effect and further determine the pathways of intramolecular charge transfer.

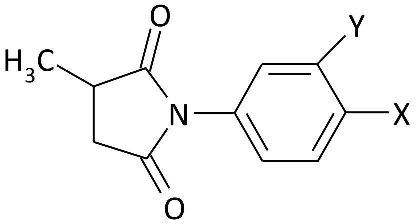

Figure 1. Chemical structure of the investigated succinimides.
(X = H, Y = H (1); X = OCH_3, Y = H (2); X = CH_3, Y = H (3); X = OH, Y = H (4); X = Cl, Y = H (5); X = H, Y = Cl (6); X = Br, Y = H (7); X = H, Y = Br (8); X = $COCH_3$, Y = H (9); X = I, Y = H (10); X = COOH, Y = H (11); X = NO_2, Y = H (12))

BS-CC P13

Structural isomers of dicyanoacetylene ions: a theoretical study

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Although cyanoacetylenes have been observed in the interstellar space, the symmetric dicyanoacetylenes have no dipole moments and are more difficult to detect, but are expected to be comparably abundant [1]; C_4N_2 is also found in the Titan's atmoshere [2].

Owing to the fact that the ions play an important role in interstellar media due to reactions of electron detachment and addition of electrons, all the possible structural isomers that have real local minima on the potential energy hypersurface of C_4N_2, $C_4N_2^+$, and $C_4N_2^-$ are reported. There were many experimental and theoretical investigations of these species. Particularly, many 'exotic' isomers of the neutral species were already theoretically predicted [3-5]; However, we apply the systematic procedure for obtaining structural isomers, and additionally, present the first theoretical prediction for the ions.

The possible isomers of dicyanoacetylene, its cation and anion, were obtained by the stochastic 'random kick' procedure, which is a derivative of the stochastic search method first reported by Saunders [6]. After random-kick procedure within a sphere of several different radius r = 0.5 – 2.0 Å, the obtained structures were then optimized using the *ab initio* methods.

Equilibrium geometries of linear, hexagonal and branched C_4N_2, $C_4N_2^+$, and $C_4N_2^-$ structural isomers are presented with their relative energies including zero-point energy corrections, using the B3LYP3 functional [7] in the aug-cc-pVTZ basis set [8]. Energies were refined by the restricted open-shell coupled cluster calculations [RCCSD(T)] [9] with correlation of valence electrons. These methods are incorporated in MOLPRO 2012.1 program package [10]. We report ionization energies and electron affinity of important neutral isomers.

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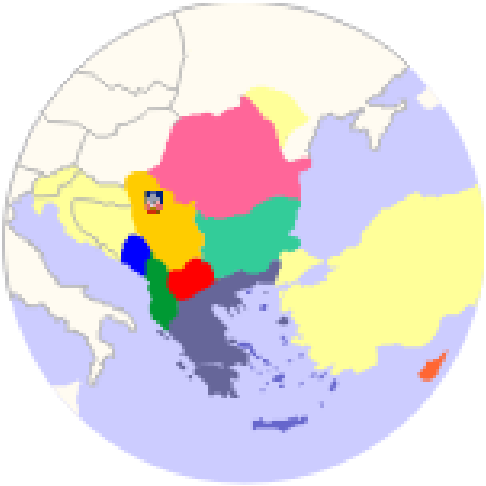

Electrochemistry

O 16 BS-EC

Oxygen reduction and ethanol oxidation on polycrystalline Pt surface in 0.1 M H_2SO_4 in mixed H_2O - 10 vol.% DMSO solvent

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Over the last several decades oxygen reduction reaction (ORR) in aqueous solutions occupies attention of the electrochemical community, mainly due to the large impact in the fields of fuel cells and metal-air batteries. By reduction on Pt surface, O_2 converts itself to water or hydroxyl ion [1,2]. In aprotic solvents, the kinetics of reduction was found to depend on the nature of both the electrode material [3] and the solvent [4]. Besides ORR, Pt electrocatalysts are used to catalyze some other electrochemical reactions such as low-molecular weight organics [2]. Hence, any modification of Pt surface in resulting in highly active and selective catalyst for specific purpose is of great interest. In this contribution, dimethylsulfoxide (DMSO) was investigated as a modifier of platinum electrocatalytic activity. Electrochemical measurements were performed using polycrystalline Pt (Pt-poly) disk electrode in mixed H_2O-DMSO solutions supported by 0.1 mol dm^{-3} H_2SO_4. Electrolytic solutions contained up to 10 vol. % of DMSO. Cyclic voltammetry experiments performed in de-aerated solutions pointed out that Pt surface oxidation and bisulfate adsorption are hindered by competitive adsorption of DMSO. By potentiodynamic polarization, DMSO adlayer was found to be stable up to approx. 0.9 V *vs.* saturated calomel electrode. When Pt-poly electrode with adsorbed DMSO layer on its surface was exposed to deep anodic polarization in an aqueous solutions with no DMSO added, electrode surface was oxidatively cleaned and cyclic voltammogram of clean Pt-poly was recovered. Formation of DMSO adlayer affected the electrocatalytic activity of Pt-poly electrode. Namely, voltammetry in O_2-saturated solutions indicated that ORR onset potential was shifted to more positive potentials, while at higher cathodic overvoltages ORR kinetics was somewhat hindered in the presence of DMSO. Nevertheless, compared to the DMSO-free aqueous H_2SO_4 solution, in the solution containing 1 vol. % of DMSO higher ORR specific activity of Pt electrode was measured. It was confirmed also that the adsorption of DMSO blocks ethanol oxidation reaction in the entire potential window where ORR takes place. This indicates that modification of Pt surface by DMSO adlayer could prevent problems related to ethanol cross-over in Direct Ethanol Fuel Cells. This offers a general route to obtain highly selective electrocatalytic surfaces by use of the modifiers based on strongly adsorbing molecules.

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O 17 BS-EC

RuO_2–SnO_2 as a Pt catalyst support in methanol electrooxidation reaction

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Current electrocatalysts for polymer electrolyte membrane fuel cells (PEMFCs) are Pt or Pt-alloy nanoparticles supported on carbon blacks. Role of the catalysts' support is to provide fine dispersion of catalyst particles. The support must have high electrical conductivity and high stability under the fuel cell operating conditions. Main drawback of carbon blacks is their insufficient corrosion resistance, which has been recognized as one of the causes of performance degradation of PEMFCs [1]. Therefore, there is a need for finding new materials that could replace carbon supports. Metal-oxide ceramics distinguish themselves as a promising candidate due to their high stability in acid media. In the present study Ru-doped SnO_2 was synthesized and used as a support of Pt nanoparticles. On this material the methanol oxidation reaction was investigated in order to estimate its suitability for application in the direct methanol fuel cell (DMFC).

Doping of SnO_2 with a foreign metal increases its conductivity. Ru was chosen because it is suspected that both SnO_2 and RuO_2 interact with Pt, enhancing its catalytic performance. The Ru-doped SnO_2 powder (RuO_2-SnO_2) was synthesized through modified hydrazine reduction method [2]. Pt nanoparticles were deposited on the support by a conventional borohydride reduction method. The physicochemical characteristics of the RuO_2-SnO_2 and Pt/ RuO_2-SnO_2 were studied by X-ray diffractometry, energy dispersive X-ray spectroscopy and transmission electron microscopy. RuO_2-SnO_2 powder has rutile structure with the grain size of 4 nm, while the average Pt particle size was 5.3 nm.

The RuO_2-SnO_2 and Pt/RuO_2-SnO_2 powders were applied on a glassy carbon substrate in the form of a thin-film. The electrochemical characterization was performed in 0.10 M H_2SO_4 saturated by N_2. The results were compared with the commercial Pt/C and PtRu/C catalysts. Cyclic voltammetry of Pt/RuO_2-SnO_2 indicated good conductivity of the supporting material and displayed usual features of Pt. The electrochemically active Pt surface area was determined by oxidation of pre-adsorbed CO. Oxidation of CO_{ads} on Pt/RuO_2-SnO_2 starts at less positive potentials than on PtRu/C and Pt/C. Methanol oxidation was investigated in the electrolyte containing 0.5 M CH_3OH by recording potentiodynamic polarization curves at a sweep rate of 50 mV s^{-1} and chronoamperometric curves at the potential of 0.5 V vs. RHE. The results obtained by both methods indicate higher initial current values of methanol oxidation on the Pt/RuO_2-SnO_2 catalyst in comparison to commercial PtRu catalyst, but greater loss in current with time.

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BS-EC P01

Inhibitive properties of thiazole derivative on the corrosion of copper in acidic media

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Corrosion of materials causes significant losses in the economy of each country, which is why, belongs to the important factors of the global financial and energy crisis. At the same, one of the major sources of material losses is corrosion of metals. Corrosion protection of metals is achieved in a different ways. In this study the possibility of using thiazole derivative, 5-(4'-isopropylbenzilidene)-2,4-dioxotetrahydro-1,3-thiazole (IPBDT), as a potential inhibitor of copper corrosion in acidic solution (0,1 moldm^{-3} H_2SO_4) was investigated. The inhibition efficiency of the investigated compound in a function of concentration was determined by potentiostatic polarization measurements, and also the mechanism of its adsorption on the copper surface. It was found that in the investigated range of concentrations, increase in concentration of IPBDT results in better inhibition efficiency. Furthermore, it was noticed that the examined derivative acts as a mixed inhibitor on the corrosion of copper in acidic media. It is concluded that IPBDT adsorbed on the metal surface by the mechanism of Langmuir adsorption isotherm. Based on the obtained isotherm, the constant of the adsorption process (K_{ads}) and standard free energy of adsorption ($\Delta G°_{ads}$) of investigated inhibitor was calculated. Obtained value of constant of the adsorption and standard free energy of adsorption, indicated that adsorption process of investigated thiazole derivative on copper surface is fast, spontaneous and adsorption layer formed on copper surface is stabile.

BS-EC P02

Salicylaldoxime as effective copper and brass corrosion inhibitor in artificial seawater

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The effect of salicylaldoxime on corrosion of copper and brass in artificial seawater was studied applying electrochemical methods. Seawater is highly corrosive media, and also widely spread [1-3]. Salicylaldoxime and its derivatives are primarily used as extraction reagent [4-6]. According to literature data salicylaldoxime can have an inhibiting effect on copper corrosion [7], alluminium alloy corrosion [8] and alluminium and zinc pigments corrosion [9]. However, there are no results published regarding its effect on brass. Also there are no data of the examination of its efficiency in seawater. Electrochemical polarization data indicate that it can be used as an inhibitor of those metal and alloy corrosion inhibitor, whereas it has more pronounced influence on brass electrochemical corrosion. It is known that salicylaldoxime forms complex with Cu(II) ions [7] formed upon anodic polarization of copper and its alloys, so the mode of action probably includes that reaction and the formation of the protective layer. The mode of adsorption was examined and Langmuir adsorption isotherm was found to be appropriate to describe that process, whereas the value of Gibbs free energy of adsorption, which is calculated to be around 30kJ/mol, lies in the area between strictly physical and chemical adsorption.

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BS-EC P03

Microstructure and corrosion behavior of Zn-Mn alloys electrodeposited from chloride and sulfate electrolytes

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Among various zinc alloys, Zn-Mn alloy coating has received wide attention in the automotive industry, due to its attractive features. The large-scale production of Zn-Mn coatings with varying Mn content seems achievable by electrochemical deposition. However, the incorporation of higher Mn percent in the alloy is a difficult issue, since the standard electrode potentials of the Zn^{2+}/Zn and Mn^{2+}/Mn couples are significantly different. One way to overcome this issue is to shift the deposition potential of Zn closer to that of Mn, by using a complexing agent. The two new types of electrolytes for Zn-Mn alloy deposition, namely, simple chloride electrolyte with H_3BO_3 and simple sulfate electrolyte with $(NH_4)_2SO_4$ seem as good candidates for a commercial production of Zn-Mn coatings. So, the scope of the present work was to investigate the influence of the electrolyte type (chloride vs. sulfate) on the characteristics of the Zn-Mn alloys electrodeposited under the economically favorable conditions: room temperature, low deposition current density (c.d.), and without additives. The Zn-Mn alloys were obtained at constant c.d., and potential-time curves were recorded during the deposition. Electrodeposits were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), and atomic absorption spectrophotometry (AAS). It was found that Zn^{2+} and Mn^{2+} ions reduction occurred at higher overpotentials in sulfate bath, leading to higher Mn content in the deposits and smaller crystallites as compared to the chloride electrolyte. AFM images of deposits revealed that with the increase in deposition c.d., bigger agglomerates formed in both electrolytes, leading to higher roughness and heterogeneity of the samples. So, the Zn-Mn coatings were deposited at c.d.s of up to 80 mA cm^{-2} because at higher c.d.s the samples from sulfate electrolyte were non adherent and dendritic. Depending on the deposition c.d., the XRD patterns of the Zn-Mn deposits produced from chloride electrolyte indicated that the coatings were formed of either η- or ε-Zn-Mn phase, while the coatings obtained from sulfate bath consisted of ε-Zn-Mn phase. The linear polarization method showed that Zn-Mn alloys deposited from sulfate electrolyte exhibited higher corrosion resistance in NaCl corrosive media.

BS-EC P04

The process of stabilization of K_2FeO_4 which is produced electrochemically
Postupak stabiliacije K_2FeO_4 proizvedenog elektrohemijskim postupkom

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In this work was examined efficiently and relatively simple method of stabilization K_2FeO_4 which is produced electrochemically [1]. Stabilization of K_2FeO_4 slows or almost completely stops chemical decomposition of K_2FeO_4, which allows the storage of a much longer period of time, facilitating the commercialization and widespread application K_2FeO_4 in materials, environmental engineering, chemical synthesis and electrochemical power sources [2].

The essence of the process of stabilization of ferrate (VI) is in application of potassium ions in the rinsing of crystalline phase K_2FeO_4. As K_2FeO_4 is very soluble in water and is susceptible to decomposition according to the reaction, $4K_2FeO_4 + 10H_2O \rightarrow 4Fe(OH)_3 + 8KOH + 3O_2$, it is necessary to use highly concentrated wash solution so that potassium ions can move the equilibrium, preventing dissolution K_2FeO_4. Experiments have found that rinsing solution should contain at least 30 % of potassium salts and a pH value greater than 9. The residual potassium salt in the crystal phase K_2FeO_4 does not present problem for the stability of ferrate, on the contrary, if potassium phosphate is used it will further stabilize both solid and liquid phase ferrate. These phosphate salts and phosphate ion build complexes with ions which catalyze the reaction of decomposition ferrate (FeO_4^{2-}) ions, which further stabilize K_2FeO_4.

Verification of the stability of the obtained salts K_2FeO_4 was made by chromate analytical method. Measurements were performed at regular intervals to determine the stability of treated and untreated ferrate.

Acknowledgement: *The authors would like to thank to the Ministry of Education and Science of Republic of Serbia (Project No. TR 34025) for their financial support.*

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BS-EC P05

A kinetic study of electrochemical decolorization of arylazo pyridone dyes

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Electrocatalytic decolorization of arylazo pyridone dyes (Fig. 1) was investigated in the presence of NaCl using DSA Ti/PtOx electrode in diluted NaOH. Decolorization can be attributed to the indirect oxidation of the investigated dyes by the electrogenerated hypochlorite ions formed from the chloride oxidation. Decolorization has been investigated for different sodium chloride concentration in the range from 10 g dm^{-3} to 40 g dm^{-3}, agitation speed in the range from 150 to 500 rpm, currents in the range of 100 to 250 mA, and dye concentration from 5 to 20 mg dm^{-3}. There is a significant effect of agitation speed on the decolorization rate between 150 and 325 rpm with a negligible effect after 325 rpm. The rate constant increases with increasing salt concentration up to 30 g dm^{-3}. At higher concentration, namely at 40 g dm^{-3} small decrease in the reaction rate was observed. Increase in dye concentration decrease the reaction rate, while above the concentration of 10 mg dm^{-3} there is a small, almost negligible decrease in the electrocatalytic rate of decolorization. Above 200 mA the rate constant deviate from the linearity probably due to the direct oxidation of the dye on the electrode surface. Optimum electrolyte should contain ~30 g dm^{-3} NaCl, and electrolysis parameters will be as follows: current 200 mA (400 mA dm^{-3}) with the reaction voltage of 3.35 V. The effect of substituents on the reaction rate was also studied. It was concluded that the electron-accepting substituents inhibit the reaction, while electron-donating substituents promote the reaction.

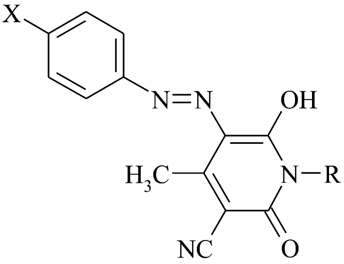

Figure 1. Structure of 5-arylazo-3-cyano-6-hydroxy-4-methyl-2-pyridones (X = OCH_3 (1), OH (2), NO_2 (3), H (4), $COCH_3$ (5), CH_3 (6), COOH (7), Cl (8), Br (9), CN (10); R=CH_2CH_2OH); X= OCH_3 (11), R=H; X= OCH_3 (12), R=CH_2CH_3).

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BS-EC P06

Effect of Mn and V on hot corrosion of TiAl-alloy

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Molten salts are promising medium for a new generation of nuclear reactors and/or for the treatment of spent nuclear fuel. One of the most important problems related to the industrial application of this idea is a development and testing of suitable materials which can resist corrosion attack of molten salts. We have chosen for this work the eutectic mixture of alkali metal chloride-fluorides as a model medium for corrosion studies. The effect of Mn and V on hot corrosion of TiAl-based alloy in the molten eutectic KCl-LiF-NaCl (37-13-50 mol%) at 903 K has been investigated. The morphology of the Ti-Al-X (X=Mn or V) was observed by micrography, XRD and SEM before and after the corrosion process. Information on the exposed surface in the electrolyte and the relative atomic concentration were obtained by XPS analysis method. The corrosion measurements were carried out in a resistor heated vertical furnace in argon atmosphere using polarization measurements. The corrosion parameters (polarization resistance, corrosion current, potential and rate) were calculated and the obtained results were correlated with the micrographic images of the studied samples (before and after corrosion process).The corrosion process take place by forming a passive film and the corrosion products were identified as metal oxides.The results show that for both studied alloys TiO_2 is the main phase.The Ti-Al-Mn alloy have a low hot corrosion rate (0.0278 mm/year) because the outer layer of the scale is mainly protective Al_2O_3, while Ti-Al-V have a strong increases hot corrosion rate because of the presence of TiOCl and low concentration of Al_2O_3 (due to the presence of V_2O_5 which can induce acidic dissolution of Al_2O_3). In the same time in this alloy the quantity of TiO_2 is smaller. Binding energies and chemical compounds of both alloying metals in both alloys before and after corrosion were tabulated. As a result, the scale of hot corrosion resistance for the studied alloys is TiAlMn >TiAlV. In fact we can conclude that we can recommend TiAlV for use at lower service temperatures.

***Aknowledgment**: This contribution was carried out within the research programme „Electrode processes, new materials for electrochemical systems and corrosion" of the "Ilie Murgulescu Institute" of Physical Chemistry, financed by the Romanian Academy*

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BS-EC P07

Effect of magnetization state on the corrosion behaviour of NdFeB permanent magnets

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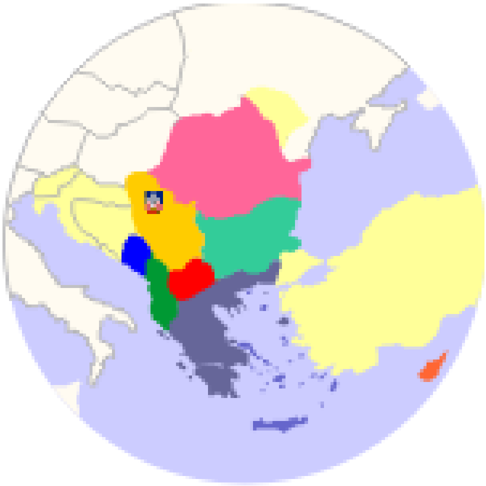
Due to their excellent magnetic properties NdFeB permanent magnets are widely used in tehnological applications.The microstructure of the NdFeB sintering magnets presents the ferromagnetic $Nd_2Fe_{14}B_4$ grains surrounded by paramagnetic Nd-rich intergranular phase. The magnetic properties of the NdFeB before corrosion were studied by ponderomotive method in 0.86 T magnetic fields in 77 – 800 K temperature range. It is shown what specific magnetisation temperature dependences are reversible in such temperature interval, and it permit to make a conclusion about magnetic properties stability $\leq$ 800 K. At 77 K the σ value is equal ~ 140 $A \cdot m^2 \cdot kg^{-1}$.The corrosion of uncoated NdFeB magnets in the non-magnetized (NM) and magnetized (M) state was comparatively investigated in 3.5 % NaCl solution by potentiodynamic polarization experiments. The corrosion parameters (R_p, i_{corr}, E_{corr} ,CR) were calculated and the obtained results were correlated with the micrographic images of the studied samples (before and after corrosion). It was observed that the magnetization has a positive influence on the corrosion resistance of the NdFeB samples; the corrosion rate was found to be 0.688 mm/year for the NM-state and 0.276 mm/year for the M-state of the NdFeB sample, while both of them have an E_{OCP} =-0.747V. XRD was performed for both samples and SEM/EDS for the NM sample(before and after the corrosion process) and the coresponding chemical composition (wt%) was calculated.The XPS survey spectra for the NM-state of the NdFeB sample before/after corrosion were recorded for the most prominent transitions: O, Fe, Nd, B and C .From the calculated results, substantial amounts of C were detected on surface, which may be attributed tothe fact that the surface of the samples was contaminated with unavoidable carbon from CO_2 and hydrocarbon adsorbed on the outermost layer from ambient atmosphere. High resolution spectra for the Fe2p, Nd3d, Nd4d and B1s for the initial and corroded were plotted and from these spectra we can conclude that all the elements of the NdFeB corroded alloy are present in an oxidized form (Nd_2O_3, Fe_2O_3 , B_2O_3). The fact that we have the Nd4d transition on the spectra indicates that the Nd signal came from the volume of the sample. The passive film composition is apreciated to be of oxides and this composition is stable at the surface (first 10nm) and in the interior of the alloy (bulk) in different concentrations. Due to their composition of highly reactive components and complex microstructure NdFeB magnets exhibit a low corrosion resistance and need to be protected by some special anticorrosive layers

***Aknowledgment**: This contribution was carried out within the research programme „Electrode processes, new materials for electrochemical systems and corrosion“ of the "Ilie Murgulescu Institute" of Physical Chemistry, financed by the Romanian Academy and within the bilateral project „The influence of corrosion process on Nd-Fe-B structure and magnetic properties“ Romania-Belarus for 2012-2013.*



Materials Chemistry

O 18 BS-MC

Asymmetric polyethersulfone membranes with crosslinked poly(glycidyl methacrylate) particles

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Polyethersulfone (PES) is frequently used for high-performance ultrafiltration membranes. Functionalization of PES membranes is required to introduce new groups for specific applications, such as affinity membranes for bioseparations [1]. Functionalization methods include bulk modification of PES material, blending of PES with another material, or surface modification of PES membranes [2]. In this work a novel method for introducing functional groups in asymmetric PES membranes is presented [3]. A cast film comprising PES, glycidyl methacrylate (GMA) and a common solvent was exposed to UV irradiation to form a gel of crosslinked polyGMA. The gel was then immersed in a water bath to create an asymmetric membrane with crosslinked polyGMA particles, as shown in Fig. 1. A simple treatment of these membranes with diethylene triamine was used to open the epoxide rings in polyGMA particles and introduce amine functional groups. The effects of monomer concentrations on the properties and separation performance of these novel membrane adsorbers will be presented.

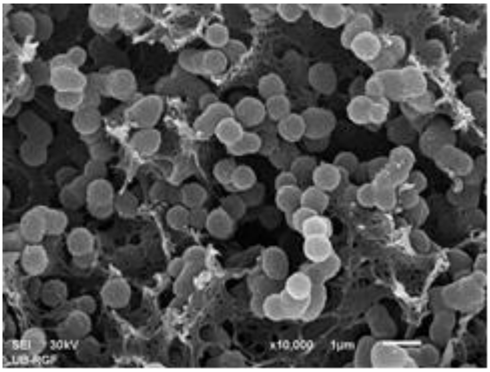

Fig. 1. SEM micrograph of a cross-section of a PES membrane with crosslinked polyGMA particles.

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O 19 BS-MC

Anomalous iridium, arsenic, zinc, antimony and soot in the ejecta layers at Cretaceous-Paleogene boundary: A mass of submicron fraction in the Chicxulub impact vapor plume

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The fireball plume of the Chicxulub impact event at the Cretaceous-Paleogene boundary was probably mostly composed of vaporized material emitted into the atmosphere (stratospheric level) by the impact. Most of this vapor was dispersed globally and condensates, creating a thin so-called ejecta layer. Recent thinking proposes that the impact vapor plume contained minimal amounts of submicron-size particles (dust) 10^{13} g - 10^{14} g insufficient to suppress photosynthesis. However, it seems that the global abundances of the impact-derived iridium, arsenic, zinc, anthimony and soot coupled with observations do not support this interpretation.

O 20 BS-MC

Cretaceous-Paleogene boundary clays from Spain and New Zealand: iridium and arsenic anomalies

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Remarkably high arsenic (As) contents have been reported in numerous Cretaceous-Paleogene boundary (KPB) clays worldwide including that from Spain (at Caravaca and Agost) and New Zealand (at Woodside Creek). The two interpretations have been offered to explain this anomaly. The first one suggests that this As was generated by combustion of fossil fuels (such as crude oil, coal or oil shales) near the Chicxulub impact site and the second interpretation recalls the post-impact combustion of the global biomass at the KPB. Both types of combustion were presumably triggered by the Chicxulub impactor. This report shows that the estimated surface densities of As in Spain and New Zealand strongly contradict the fossil hydrocarbons/biomass hypotheses. It is also appeared that anomalous As in the boundary clays in these two regions was not sourced by the enormous Deccan Trap volcanism.

O 21 BS-MC

Novel negatively-charged ultrafiltration membranes made by a combination of immersion precipitation and photopolymerization

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Ultrafiltration (UF) membranes are currently used in industry for the concentration of proteins and other macromolecules. Performance of UF membranes is generally limited by a trade-off between permeability and selectivity [1]. However, electrically-charged ultrafiltration membranes can provide a dramatic improvement in ultrafiltration performance [2]. Novel UF membranes were made by combining traditional immersion precipitation process for making membranes with photopolymerization of the casting solution comprising polyethersulfone, glycidyl methacrylate and other reactive monomers. Negative charges were introduced either by initially using 2-acrylamido-2-methylpropane sulfonic acid as a reactive monomer, or were later created by epoxide ring opening of crosslinked glycidyl methacrylate. As shown in Fig. 1, selectivity of these membranes significantly improved as the concentration of negatively-charged groups in the membrane increased. The effects of membrane composition on the properties and separation performance of these novel UF membranes will be presented.

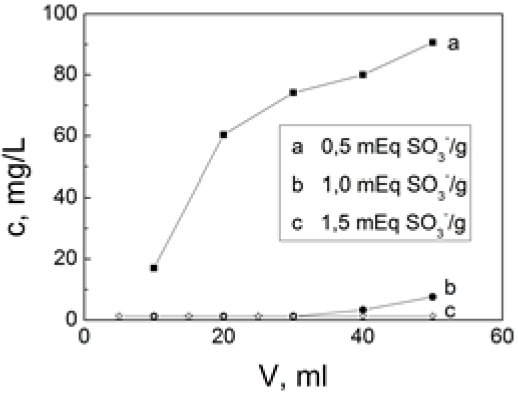

Fig. 1. Permeate concentration of Orange Basic 28 dye as a function of the volume filtered through negatively-charged UF membranes.

This work has been funded by Serbian Ministry of Education and Science within the framework of the projects TR32008, III 43009 and OI 172062.

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BS-MC P01

Liquid crystalline behavior of new pyridine based bent-core mesogens: a structure–property relationship study

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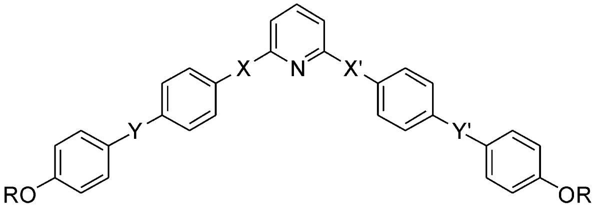
Three series of new symmetrical bent-core mesogens with 2,6-disubstituted pyridine as central unit were synthetized (Fig. 1). In the five phenyl rings containing compounds, different connecting groups (amide (–CONH–), ester (–COO–), azomethine (–CH=NH–) and olefinic (–CH=CH–)) were used. The symmetrical terminal groups differed in their chain lengths. The chemical structures were confirmed by FTIR, ^{1}H and ^{13}C NMR spectroscopy. The liquid crystalline phases formed by these compounds were investigated by polarizing microscopy and differential scanning calorimetry. In general, the clearing temperatures decrease with elongation of the terminal chains. The most stable compounds with the lowest clearing temperatures were obtained by combining the ester linkage with the olefinic group (series III). Regarding the significant π-conjugation level of the presented bent-core mesogens, it is expected that they have advanced electro-optical properties and potential application as organic electronic materials.



Compound	X	X'	Y	Y'	R
Ia	CONH	NHCO	CH=N	N=CH	C_5H_{11}
Ib	CONH	NHCO	CH=N	N=CH	C_7H_{15}
Ic	CONH	NHCO	CH=N	N=CH	$C_{12}H_{25}$
IIa	OOC	COO	N=CH	CH=N	C_5H_{11}
IIb	OOC	COO	N=CH	CH=N	C_7H_{15}
IIc	OOC	COO	N=CH	CH=N	$C_{12}H_{25}$
IIIa	CH=CH	CH=CH	COO	OOC	C_5H_{11}
IIIb	CH=CH	CH=CH	COO	OOC	C_7H_{15}
IIIc	CH=CH	CH=CH	COO	OOC	$C_{12}H_{25}$

Figure 1. *Chemical structures of the investigated bent-shaped mesogens*

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BS-MC P02

Study of the influence of phase inversion parameters on the porosity of polymer bicomponent membranes

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According to literature, phase inversion is a very often used technique for membranes preparation [1]. Polyacrylonitrile is widely used for membranes obtaining due to its inherent features (high stability, chemical resistance, physical strength) [2].

The aim of the present work was to prepare bicomponent polymer membranes using an acrylonitrile-vinyl acetate (AN-AV) with an AN/AV percentage gravimetric content of 70/30 in mixture with polyvinyl alcohol (PVA). The copolymer was synthesized, using a redox initiation system (potassium persulfate-sodium metabisulfite), at 45 ^{0}C in N_2 atmosphere.

Membranes preparation was achieved in two stages. In the first stage, it was prepared a solution dissolving the copolymer together with PVA in DMSO. In the second stage this solution was casted on glass plate, followed by the immersion of this plate in water- iso propyl alcohol mixture (W-IzOH). There were used different W-IzOH mixtures. It was studied the effect of IzOH amount on the composition (by FTIR-Fourier Transform Infrared spectrometry) and on the porosity of membranes (by OM-optical microscopy).

The OM images show that an increase in the IzOH amount in the coagulation bath leads to a porosity decrease. FTIR spectra show that for higher IzOH volumes, the peak from 3400 cm^{-1} (assigned to –OH groups) is more intense.

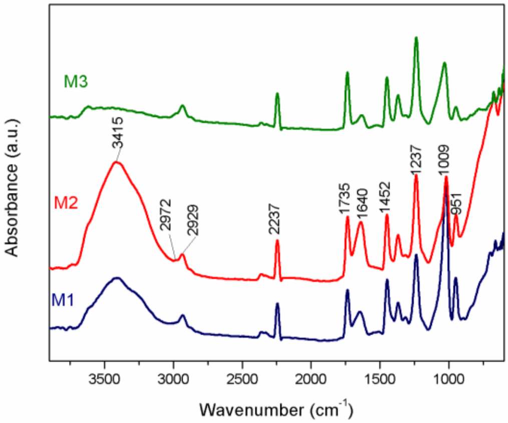

Fig. 1. FTIR spectra of three membranes prepared using the same polymer mixture but different coagulation mixtures

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BS-MC P03

Thermal properties of modified urea-formaldehyde resins with SiO_2 and wood flour

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Wood flour and plastics composites (WFPCs) attracted a great interest in recent years owing to their relatively good properties and the lower costs. Today, attention has been focused on the nano-composites, especially those obtained from layered silicates in thermoplastic or thermosetting matrices since they demonstrated a noticeable improvement in thermal and mechanical properties with respect to micro-composites such as wood floor. Wood polymer composite (WPC) covers a wide range of area in composite field [1]. These are eco friendly, low cost consuming, biodegradable, and renewable. The consumption of plastic materials has increased enormously due to their various advantages. In the polymer composites, different types of fillers are used for improving the thermal, mechanical as well as other properties. Urea–formaldehyde (UF) resin is a polymeric condensation product of the chemical reaction of formaldehyde with urea, and a kind of amino resin. UF resins are most widely used for the manufacture of wood-based composite panel such as plywood, particleboard, or medium-density fiberboard. As a typical amino resin, UF resin adhesive possesses some advantages, such as fast curing, good performance in the panel, water solubility, and lower price [2]. Wood itself is a complex, three-dimensional, polymer composite made up primarily of cellulose, hemicelluloses, and lignin [3,4]. These three hydroxyl-containing polymers are distributed throughout the cell wall. In this study, the thermal stability of modified urea-formaldehyde resin - UF resins with silicon dioxide (SiO_2) and wood flour (WF) (Pinus silvestris L.) as fillers was investigated by thermo-gravimetric analysis (TG), differential thermal gravimetry (DTG) and differential thermal analysis (DTA) supported by data from IR spectroscopy. The shift of DTG peaks to a high temperature indicates the increase of thermal stability of modified UF resin with SiO_2 and WF which is confirmed by the data obtained from the FTIR study. The incorporation of nano-silica in wood flour/polymer composite significantly improved the thermal stability.

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BS-MC P04

Novel reactive monomers bearing a push-pull azo-moiety

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Azo-polymers are one of the most investigated classes of photo-responsive materials [1], on account of the numerous applications given by their interesting properties, such as: nonlinear optical response, photo-controlled reversible property changes, photo-induced birefringence, and dichroism [2]. Depending on the targeted application, certain aspects are to be tackled in order to exploit azobenzene unique behavior, i.e. type of azo-dye and polymer matrix, nature of bonding of the chromophore to the matrix, incorporation strategy, chromophore load, [3, 4].

Radical (co)polymerization of azo-monomers is one of the most attractive methods used to covalently attach an azo-moiety to a polymer matrix [3]. This method is preferred for its simplicity and control upon the feed ratios, but on the other hand, it implies the synthesis of reactive monomers bearing the azobenzene unit. Consequently, an azo-monomer should possess an optimum length of the flexible spacer that joints the azo moiety to the polymer backbone, since the dynamics of the side chain depends on the degrees of freedom of the azo groups, and has an impact on the overall optical properties of the final material [5].

Herein, the synthesis and characterization of two monomers bearing a push-pull azo-moiety, starting from a pseudo-stilbene type azo dye, is presented. The reactivity of these azo-based methacrylate monomers is highlighted since they are capable to easily undergo free radical homo-polymerization. The resulting homo-polymers possess the azo-moiety covalently linked through a flexible spacer to the backbone. All resulted structures are characterized by means of FT-IR, NMR spectroscopy and elemental analysis, whereas the obtained homo-polymers are characterized by TGA and SEC analysis.

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BS-MC P05

Synthesis and characterization of membranes based on chitosan modified by organoclay

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Chitosan is a natural polymer, hydrophyllic and biodegradable polysaccharide. Chitosan can easily form films and membranes that can be used in the pharmaceutical industry, for the adsorption of metals and other compounds from water and are therefore interesting from the point of view of environmental protection. Combining chitosan with clay can lead to improvements in their properties because it reduces the hydrophilicity of chitosan which expands the scope of their application.

In this paper the membranes based on chitosan modified by montmorillonite-poly (vinyl pyrrolidine) in different ratios of reactants, up to 50% of clay, and crosslinked with glutaraldehyde are presented. The membranes were characterized by FTIR spectroscopy, swelling behaviour in water and methanol and conductivity determined by four points method. The highest water adsorption is present at membranes with 30% of clay, whil the conductivity increases with the increase of montmorillonite amount.

The authors acknowledge funding from the Ministry of Education, Science and Technological Development of the Republic of Serbia, Science Projects No. 43009 and 172062.

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BS-MC P06

Synthesis and characterisation of hybrid hydrogels based on poly(methacrylic acid) and casein and their application in removal of dyes and heavy metal ions

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Hybrid hydrogels based on poly(methacrylic acid) (PMAA) and casein have been synthesized via free-radical polymerization. Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Dynamical-mechanical Analysis (DMA), as well as swelling experiments were conducted to investigate the effects of the synthesis parameters: the amount of incorporated casein (0-30 wt%), neutralization degree of methacrylic acid (0-100%) and concentrations of crosslinker (0.3-0.8 mol%) and surfactant (0-1 wt%), on structure and the behaviour of derived hydrogels. Combining well the strong interaction between PMAA/casein and cationic species, accessibility of active sites in swollen network and fine mechanical stability, prepared hybrids are considered as promising candidates for removal of cationic species from an aqueous solution. Ni (II) ions are used as model metal ions, while basic yellow 28, basic red and methylene blue are used as model dye molecules. Adsorption processes are found to be highly dependent on composition of hybrid hydrogels, the initial concentration of pollutant, solution pH and sorbent mass. Langmuir, Freundlich and Dubinin-Radushkevich sorption isotherms were applied on equilibrium adsorption data. Adsorption processes are found to be favourable with removal efficiency of nickel (II) ions higher than 95%. Very good adsorption properties even at initial Ni (II) concentrations lower than 1 ppm makes these low-cost materials highly sensitive adsorbents suitable for practical use in real conditions.

BS-MC P07

The effect of silver nanofillers on the thermal properties of polystyrene

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Nanocomposites (NCs) comprised of metal nanoparticles (NPs) embedded in polymer matrices usually exhibit a simple combination of the physical properties of the polymer, along with the specific optical or electrical characteristics associated with the NPs. However, novel behavior can arise thanks to synergistic effects between the NPs and polymer matrix. The present work represents the continuation of our study on the interaction between silver nanoparticles (Ag NPs) and polystyrene (PS) matrix that govern the properties of polymer. Namely, in order to achieve homogeneous distribution of Ag NPs in the PS matrix, the *in situ* bulk radical polymerization of styrene was performed in the presence of monodisperse surface modified Ag NPs. The influence of the presence of Ag NPs and their concentration on the glass transition temperature and thermal stability of PS matrix was investigated in details using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) performed in argon and air atmosphere. The results indicated that thermal and thermo-oxidative stability of PS were improved upon incorporation of Ag NPs. The Ag/PS NCs have lower glass transition temperatures than neat PS because loosely packed oleylamine molecules at the interface caused the increase of free volume and chain segments mobility near the surface of Ag NPs.

BS-MC P08

Transient thermal characteristics of cellulose knitted fabrics

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The very first sensation arising from the contact between the human skin and textile material is the result of instantaneous heat exchange between these two surfaces. The warm or cool feeling depends on the contact interface between the skin and the fabric which in turn was influenced by many structural parameters like fiber type or yarn and fabric structure. Thermal diffusivity and thermal absorptivity are the parameters describing the transient thermal behavior of textile materials. Thermal diffusivity is an ability related to the heat flow through the air in the fabric structure in a direction normal to the fabric's surface. Thermal absorption is a surface-related property of textile material describing warm-cool feeling of the material. The fabric with a low value of thermal absorption means a warm feeling at first contact, whereas a high value refers to a cool feeling. These parameters are the "real" textile characteristics since they depend neither on the temperature gradient between the fabric and skin, nor on the measurement time.

The aim of this study was to evaluate the transient thermal characteristics of plain cellulose knitted fabrics. Although it is generally known that cellulose textile materials provide a cooler feeling as a consequence of the high equilibrium humidity of cellulose fibers, for our study the idea was to investigate the influence of both yarn surface and core geometry on transient thermal characteristics. Plain knitted fabrics were produced from the two-assembled hemp, cotton and viscose yarns so as to obtain five different cellulose fiber content knits. They were produced under controlled conditions in order to obtain as similar as possible construction of the knits. Bearing in mind the fact that thermal diffusivity and thermal absorptivity can be defined by means of two other thermal characteristics of textile material (thermal conductivity and thermal capacity) and the material density, these inherent parameters of the plain cellulose knitted fabrics were determined. Starting from these parameters, transient thermal characteristics were calculated indicating some differences among the knitted fabrics tested. As a consequence of the highest thermal conductivity, the hemp/cotton knit exhibited the highest thermal absorption which is presumed to cause the coolest feeling at the first contact between the skin and knit. The hemp knit which was characterized by the lowest thermal conductivity exhibited also the lowest thermal absorptivity. The highest thermal diffusivity was exhibited by the hemp/cotton and viscose knitted fabrics due to their highest values of thermal conductivity. These two knits conduct heat quickly adjusting their temperature to that of the surrounding. On the other hand, the cotton knit was characterized by the lowest thermal diffusivity due to high thermal capacity. Since the cellulose knitted fabric were comparable in basic construction characteristics, whereas the yarns were characterized by variations in fiber packing density and surface properties, the influence of yarn structure on transient thermal properties seems to be confirmed.

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BS-MC P09

Influence of abrasion on compression behaviour of woven clothing fabrics

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In the process of exploitation, woven fabrics are subjected to different mechanical effects that can cause deformation of the material depending on the type and intensity of the applied force and lead to aggravation of the starting properties of fabrics. Behavior of woven fabrics in use is the result of many different factors of which stands out abrasion resistance as one of the important criteria for comparison of the behaviour of various woven fabrics during their exploitation.

Abrasion, which is the result of external friction, occurs when the woven material comes into contact with another body - the abrasive. Depending on the intensity of the friction force, appearance of the surface of woven fabrics is changed which is reflected in the reduction of gloss, weight and thickness of the fabric, peeling up and hair growth, differences in coloration, weave masking and mechanical damage emerging. Simultaneously with these defects there is a series of invisible changes in the structure of fibers and yarns.

In this work the influence of abrasion on compression properties of clothing fabrics obtained from cotton and cotton/PES fiber blends has been examined. Fabrics were made in variants of weaves: plain, twill 1/3 and satin. Compression properties of the tested fabrics were evaluated over the size of total deformation as well as the values of reversible and residual deformation components.

Martindale's device, with a standard wool woven fabric as abrasive, was used as abrasion tool. The load of 9 kPa has been applied to the test specimen. Abrasion was realized to sample damage that is the break of two separate yarns in a test-tube. A thickness tester, used for the investigation of compression properties of woven fabrics, enabled measuring the fabric thickness at different pressures. Compression properties of the investigated woven samples were analyzed, before as well as after abrasion, in dependence of the structural parameters of fabrics (raw material composition, type of weaves used and the type of warp and weft yarn).

Based on the imposed investigations, it can be noticed an increase of the total deformation as well as reversible and residual deformation components in all samples after their abrasion, except cotton/PES woven fabric in plain weave made of folded yarn in warp and weft direction. Compression behavior of the examined woven fabrics, before as well as after abrasion, depends on the raw material composition, type of weaves and type of yarns used in the tested samples.

Acknowledgements*: This investigation was carried out within Project OI 172029 supported by the Ministry of Education, Science and Technological Development of the Government of the Republic of Serbia.*

BS-MC P10

Obtaining noble metal nanoparticles aggregates in extracts of Romanian native plants

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Metallic nanoparticles have received great attention from researchers because their biomedical benefits, for development of a new generation of nanodevices. The green obtaining methods are low cost, fast, efficient and generally lead to the formation of crystalline nanoparticles with a variety of shapes (spheres, rods, prisms, plates, needles, leafs or dendrites), with sizes between 1 and 100 nm [1-5].

In the present study metallic nanoparticles were synthesized from aqueous silver nitrate through a simple and eco-friendly route using leaf broth of basil *(Ocimum Basilicum)* and marigold (*Calendula officinalis*).

The aqueous silver and gold ions when exposed to the leaf broth were reduced and stabilized over long periods of time resulting in the green synthesis of surface functionalized silver and gold nanoparticles. The bio-reduced metallic nanoparticles were appropriately characterized.

The potential ability of this plant for the obtaining of metallic nanopartiles was investigated by spectral methods (UV-VIS absorption, FTIR, XRF, SEM).

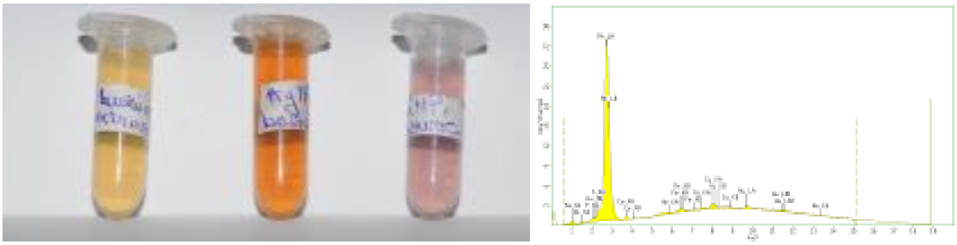

Figure 1. Left - a) Basil extract; b) AgNP-basil; c) AuNP-basil, right- XRF analysis of AuNP-marigold

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BS-MC P11

Determination of the antioxidant activity of Romanian native plant extracts

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In our days the interest in antioxidants has been increasing because of their high capacity in scavenging free radicals related to various diseases.

Marigold (*Calendula officinalis*) and basil (*Ocimum basilicum*) plants are used for long time for the treatment of different affections (asthma, bronchitis, dysentery, rheumatic pain, etc) [1-3]. The present study was conducted to evaluate the antioxidant activity of the extract solutions of methanolic medicinal plant extracts. The antioxidant activity was determined using DPPH (diphenylpicrylhydrazyl) method [4]. The results confirmed the antioxidant potential of basil (AA%=93.53) was better than marigold (AA%=90.34).

Figure 1. The marigold plant (Calendula officinalis)

Figure 2. The basil plant (Ocimum basilicum)

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BS-MC P12

Nanopores creation in silica particles for advanced separations

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Creating nanopores in different structures is a technique of high interest in many domains [1, 2]. The current work presents a robust way of creating nanopores in silica particles for applications that require advanced separations.

10 µm / 100 Å silica was used as raw material for nanopores casting. A solution of NH_4HF_2 with different concentrations (3, 4, and 5 M) was used for acidic attack of silica beads. BET method was applied in order to determine the porosity of silica before and after acidic attack and TEM method with ultrathin cut was applied to observe the morphology.

TEM images showed the formation of nanopores after the acidic attack, as can be seen in fig. 1 b) and d). BET analyses showed an increased porosity, almost three times higher in treated silica. The porosity depends on the concentration of NH_4HF_2, and this information can be used to create a desired porosity with the proper NH_4HF_2 concentration.

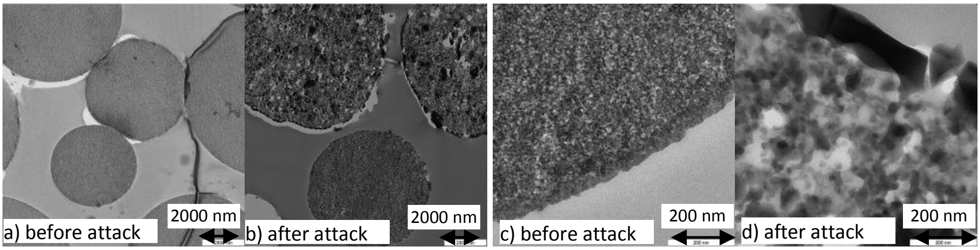

Fig. 1. TEM images of silica particles before acidic attack: a) and c) and after acidic attack: b) and d), at two different magnitude orders.

This method of nanopores creation it is robust and easy and can represent an intermediate step in many syntheses that have the purpose of silica nanocasting, molecule entrapment, pore modification, molecular sieving, molecular imprinting, and more.

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BS-MC P13

Surface modification of Fe_3O_4 nanoparticles with alkosysilanes and the miniemulsion polymerization of the formed particles

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Fe_3O_4 nanoparticles were synthesized by co-precipitation of Fe^{3+} and Fe^{2+} with NH_4OH and then, the hydrophobic modification was achieved by functionalizing Fe_3O_4 particles with different monofunctional alkoxysilanes (methyl, octyl, octadecyl and phenyl). Mini-emulsion polymerizations were performed through different initiation, in the presence of sodium dodecyl sulfate (SDS) and in different solvents (hexadecane or ciclohexane). The hydrophobic ferrite was dispersed in three monomers (styrene, divinylbenzene, butyl acrylate). The affecting factors, including stabilizer concentration, surfactant concentration, solvent concentration and the amount of Fe_3O_4, were systematically studied. Morphology, particle size, and magnetic properties of the nanoparticles were characterized by SEM, DLS, TGA and FTIR, respectively. The data show the influence of the hydrocarbon chain length of the alkoxysilanes on the final magnetic hybrids.

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BS-MC P14

Study on preparation and properties of novel functionalized polyester copolymers based on siloxanes

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Novel functionalized macroporous copolymers were synthesized by reaction of the pendant epoxy groups of poly(glycidyl methacrylate)-*co*-poly(ethylene glycol dimethacrylate)s with 1,3-bis(3-aminopropyl)tetramethyldisiloxane (TMDS) and α,ω-diamino propyl poly(dimethylsiloxane) (PDMS). It was found that the optimal conditions for the synthesis of functionalized copolymers were: reaction temperature of 80 °C, reaction time of 10 h and a mixture of *N*-methyl-2-pyrrolidone/toluene (1/3 v/v) as the solvent. The effects of the type of siloxanes and concentration of glycidyl methacrylate on the structure and properties of functionalized copolymers were investigated by solid-state ^{13}C and ^{29}Si NMR spectroscopy, FTIR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The structure of functionalized copolymers was confirmed by solid-state NMR and FTIR spectroscopy. The DSC results showed that the glass transition temperatures of copolymers were in the range from 63 to 65 °C and they slightly depend on the copolymer composition exclusively. The thermal stability was better for copolymers functionalized with TMDS in comparison with PDMS based copolymers. Thermal degradation of the synthesized copolymers starts between 276 and 290 °C. The TG curves of all copolymers display two stages of degradation at 308-368 °C (stage 1) and 395-430 °C (stage 2) which are associated with the ester and siloxane bonds. The results indicated that the thermal stability depends on the type of siloxanes and copolymer composition. The surface and cross-section morphology was investigated by SEM and the porous copolymer beads were confirmed by SEM analysis. SEM studies with energy dispersive X-ray mapping revealed that siloxanes migrate to the surface of samples due to their low surface energy. By varying the structure of siloxanes and copolymer composition, functionalized copolymers can be designed and synthesized with diverse physical properties for different purposes.

Acknowledgements. This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Projects ON 172062 and III 43009).

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BS-MC P15

A Synergy of ZnO and $ZnWO_4$ in Composite Nanostructures Deduced from Optical Properties and Photocatalysis

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A low temperature method (95°C), which involves non-ionic copolymer surfactant, was used for preparation of ZnO/$ZnWO_4$ rod-like composite nanoparticles. TEM measurements showed that particles were of nanodimensions and with rod-like shapes. The development of ZnO and $ZnWO_4$ phase was followed by optical absorption measurements. Room-temperature PL was observed for all samples, using two excitation wavelengths (270nm and 330 nm). They were characterized by band edge emission of ZnO (380 nm) for both excitations, and green emission from oxygen vacancies present in ZnO when λ_{exc} = 270 nm (4.88 eV) was used. Photocatalytical and optical properties were correlated and explained by conduction and valence band positions in our composite nanoparticles. The most effective synergy between ZnO and $ZnWO_4$ was clearly observed for nanoparticles obtained after 48 hours reaction time (Fig.1).[1,2]

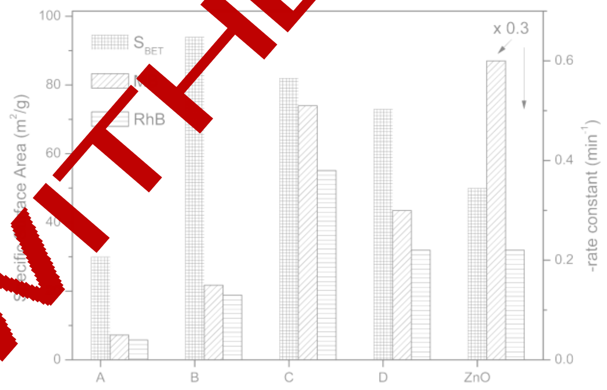

Figure 1. Specific surface area and photodegradation rate constants (for degradation of MB and RhB) of ZnO/$ZnWO_4$ powders and commercial ZnO powder.

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BS-MC P16

Adsorption of Reactive Orange 16 from aqueous solutions onto functionalized sepiolites

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The adsorption of C. I. Reactive Orange 16 dye from aqueous solutions onto natural and acid activated sepiolites functionalized with [3-(2-aminoethylamino)propyl]trimethoxy-silane was investigated using the batch adsorption method. The adsorption experiments were performed as a function of initial dye concentration, initial pH value and the equilibration time. The dye adsorption depends on the initial pH of the solution and the maximum uptake was achieved at pH 2. The capability of the Langmuir, Freundlich and Dubinin-Kaganer-Radushkevich (DKR) isotherm models to fit the experimental adsorption data were investigated and the isotherms constants were determined. The experimental equilibrium data obtained at 298 K correlated well by the Langmuir adsorption isotherm. The pseudo-second order kinetic model provides the best correlation of the experimental kinetic data. The adsorption isotherms suggested that the modification of sepiolites with [3-(2-aminoethylamino)propyl]trimethoxy-silane resulted in the formation of the adsorbents with a noticeably larger dye adsorption capacity than the natural and acid activated sepiolites. Acid activated amino functionalized sepiolite was more ***efficient than natural amino*** functionalized sepiolite.

BS-MC P17

A simple two-phase route to polyaniline/gold nanocomposites

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Combining the electrical, optical, and magnetic properties of polyaniline (PANI) with excellent chemical and physical properties of gold nanoparticles (Au NPs) is an efficient way to create novel functional nanomaterials with potential applications in biosensing and therapy, energy conversion and storage. In the present work, we report polyaniline/gold nanocomposite (PANI/Au) obtained by two-phase, water/toluene, interfacial chemical reaction. The polymerization process occurs at the interface of the organic phase (with aniline) and acidic water solution (with oxidant and Au NPs). Using this strategy, secondary growth of PANI could be suppressed. Transmission and scanning electron microscopy measurements were confirmed that PANI was formed as nanofibers decorated with 17 nm Au NPs. Characterization of the samples performed with UV-Vis and FTIR spectroscopy and XRD technique are used for description of the optical properties, interaction between components and structure of PANI/Au system. The obtained results indicate that the present synthetic route produces the PANI in conductive form (doped emeraldine salt form) with specific electric behavior, which makes PANI/Au nanocomposite suitable material for a wide range of applications.

BS-MC P18

Chemical analysis of the brick from archaeological site Mihajlovac-Clevora

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The development of chemical production is not taking place continuously, even in a narrow time interval is referred to as Late Antiquity the Eastern wing of the Roman Empire. Mihajlovac on the former Rome's main highway. Represents the border fortress (Tana), surrounding the civil settlement, as it was established archaeological excavations Mihajlovac-Klevora (Clevora), had nearly square base, the length of the walls of about 36m. The outer defensive walls were built of a combination of stone and brick. The entrance to the building was from the east. The massive construction of the walls and the remains of the pillars inside the building leading to the conclusion that the central structure was covered by the vault structure [1]. By the look of brick samples from the archaeological site Mihajlovac-Clevora, one can conclude the presence of iron and silica materials (Figure 1). Iron ions, which are components of the bricks, the characteristic red color, while the quartz material gives an inhomogeneous structure, and building materials more resistant and suitable for constructing buildings and walls. Same bricks were upgrading a stone foundation, which was 1-1.5 m high, depending on the strategic and tactical opportunities. The wall is used to prevent breaking the enemy cavalry units. Micrographs show that the brick structure moderately inhomogeneous, which means that the basic raw material for making a clay brick, red in color and quartz sand. According to Figure 2, the sample grain structure, which does not show significant inhomogenosti, but there is no rule in the geometric arrangement of particles. At higher magnification can be observed coarse quartz and other silicate mineral composition, the composition of which are carbonates, except for one minor offenses. In addition to iron and aluminum in the trace to be found, and magnesium, titanium and alkali metals as impurity substances are clay. Inhomogeneous structure is observed in the micrographs confirmed that the ceramic substance, type of bricks and can only be used for the building and are not suitable for making containers or ceramic bowl (Figure 3 and 4.). Analysis of the structure of bricks from the archaeological site Mihajlovac was performed with results and microscopic images of archaeological sites of other parts of the world, a similar period of time [2] [3].

Figure 1. The brick

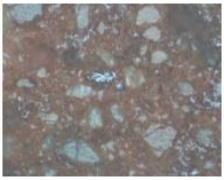

Figure 2. Micrograph

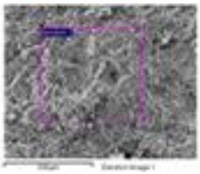

Figure 3. SEM

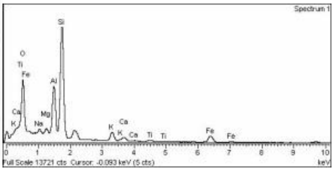

Figure 4. EDS

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BS-MC P19

Geopolymerization of fly ash as possible technology for immobilization of heavy metals from electric arc furnace dust

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Electric arc furnace dust (EAFD) is by product generated during remelting of old iron and steel scrap in the electric arc furnace which is considered as hazardous waste due to the content of heavy metals and possible dangerous impact on the environment.

There are several methods for its recycling but the most promising and cost effective is its stabilization into the construction materials through innovative method for waste stabilization – geopolymerization, [1,2].Geopolymerization process involves the chemical reaction of alumino-silicate oxides with highly alkaline activator yielding the new material with amorphous or semi-amorphous structure, called geopolymer. Immobilization of toxic materials may occur by chemical bonding, adsorption, as well as physical encapsulation but the mechanism by which heavy metal cations are incorporated into the polymer network is not yet fully understood.

The aim of this research was to investigate the effectiveness of immobilization of heavy metals from electric arc furnace dust in the fly ash based geopolymers, depending of alkaline dosage.

Fly ash is activated by alkaline solution prepared by mixing sodium silicate and NaOH solutions in a mass ratio of 1.5. Concentration of NaOH was 7, 10 and 13 mol·dm^{-3}. EAFD was added in quantity of 10 % of total solid phase. Immobilization efficacy of heavy metals from EAFD was evaluated using leaching tests TCLP Method No. 1311, EN 12457-2 for granular waste, which can be used as a criterion for defining hazardous and non-hazardous wastes for the purpose of disposal. The results indicate that increase of NaOH concentration used for geopolymer synthesis favour the immobilization of heavy metals from EAFD. Crucial point in this case is porosity of geopolymers samples.

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BS-MC P20

New structures of hydrogel nanocomposites obtained through inverse suspension polymerization

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Hydrogels are polymeric networks, made up of hydrophilic polymers and able to incorporate and retain large amounts of water [1]. The major disadvantages of the simple hydrogels consist in the higher production cost and low gel strength, leading to restriction of the agriculture and horticultural applications [2]. The mechanical strength of hydrogels can be increased by adding an inorganic reinforcing agent, mainly clays, resulting new hydrogel nanocomposites. In the present work, new hydrogel nanocomposite structures based on aminosilanes modified kaolin and cross-linked poly (acrylic acid) (PAA) were synthesized by inverse suspension polymerization for the first time. The resulting products were characterized by scanning electron microscopy (SEM), thermal analysis/ differential thermal gravimetry (TGA/DTG), Fourier transform infrared spectroscopy (FTIR) and their water absorption was assessed. The results showed that the modification of kaolinite particles with aminosilanes, led to enhanced interactions between modified kaolinite particles and PAA matrix. The SEM images of the new dried xerogel nanocomposites showed a compact and homogeneous distribution of aminosilanes modified kaolinite particles in the polymer structure. Thus, we suggest that the modification of the kaolinite particles with aminosilanes leads to an improvement in kaolinite particles dispersion inside the polyacrylic acid network. The results showed that the water absorption of the hydrogel nanocomposites synthesized strongly depended on: (i) incorporation of non - modified kaolinite particles in the polymer matrix; (ii) incorporation of modified kaolinite particles in the polymer matrix, leading to higher swelling degree; (iii) and concentration of modified kaolinite.

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BS-MC P21

Morphological characterization of polymer-based composite material

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The control of structure and the surface roughness are crucial aspects that largely determine the use of polymer-based composite materials in microcolumn in separation systems [1]. In this study, composite of macroporous monolithic copolymers of glycidyl methacrylate (GMA) and ethylene glycol dimethacrylate (PGME) [abbreviated PGME] and boehmite (in content of 5, 25 and 50 mass% with respect to monomer mixture) were synthesized by *in situ* radical copolymerization in a cast of cylindrical shape [2]. The influence of boehmite content in the reaction mixture on the morphology of composite samples was investigated by atomic force microscopy (AFM). The surface morphology has been evaluated in terms of surface roughness and fractal dimension. The surface roughness, described by root mean squared and arithmetic average values, was analyzed considering the scan scale of AFM measurements. The results show that the surface roughness increased along with scan scale for all the samples. However, the surface roughness values of the samples with alumina content of 5% and 25% were similar when scan scale was 10µm. Therefore, AFM images of samples, with scan scale of 10µm were used for fractal analysis. Fractal analysis reveals fractal nature of the surface of all samples. Fractal surface roughness of polymer-boehmite composite with 5% boehmite loading was smaller than that of samples with 25 or 50%. The fractal parameters were observed to be proportional to the surface roughness of investigated polymer-based composite materials.

Acknowledgments: *This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Projects number 172001, 172015, 43009 and III 45001).*

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BS-MC P22

Water and Dye Sorption Properties of AAm/APTAC/PEG Semi-IPN’s

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Introduction

Hydrogels are crosslinked, macromolecular polymeric materials arranged in a three-dimensional network, which can absorb and retain large amounts of water. These crosslinked polymers are capable of imbibing large volumes of water, makeing them important materials for a variety of applications in bioengineering, biomedical, food and pharmaceutical industries. Hydrogels of interpenetrating polymer networks (IPNs) consist of an assembly of two crosslinked polymers in which at least one of them is synthesized and crosslinked in the presence of the other, but there are not covalent bonds between the polymers within the network. If only one component of the assembly is crosslinked leaving the other polymer in linear form, the system is called a semi-interpenetrating polymer network (semi-IPN) [1,2].

Experimental

In this study, we have investigated the incorporation of poly(ethylene glycol), (PEG) and (3-acrylamidopropyl)trimethyl ammonium chloride, (APTAC) into acrylamide, (AAm) hydogel during free radical solution polymerization synthesis. AAm is a highly hydrophilic monomer, APTAC is cationic monomer and PEG is linear polymer. Poly(ethylene glycol)dimethacrylate (PEGDMA) was used as a multifunctional crosslinker in polymerization. The main purpose of this study was to combine both monomer and a polymer in a new polymeric system. In this respect, a series of copolymeric hydrogels were synthesized by changing the content of APTAC and PEG. Then some swelling and some diffusional parameters were investigated for swelling characterization of AAm/APTAC hydrogels and AAm/APTAC/PEG semi-IPNs [3]. Dye sorption properties of hydrogels and semi-IPNs were investigated by using anionic dye such as Calconcarboxylic acid, (CCA). Swelling and sorption studies were carried out at 25 ^{o}C [4]. For structural characterization, FT-IR analysis was made. The surface morphology of hydrogels and semi-IPNs was visualized by a scanning electronic microscope (SEM).

Conclusions

The equilibrium percentage swelling ranges are 690-1200% for AAm/APTAC hydrogels and 685-1120% for AAm/APTAC/PEG semi-IPNs. It was seen that swelling properties of AAm/APTAC hydrogels and AAm/APTAC/PEG semi-IPNs increased with the increasing of APTAC content. It was also determined that crosslinked copolymers adsorbed calconcarboxylic acid from aqueous solutions in high level.

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BS-MC P23

Effect of γ–irradiation on the hydrolytic stability of bio/inorganic modified urea–formaldehyde composites

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Urea–formaldehyde (UF) resins, as the most important type of the so-called amino plastic resins, are widely used to modify properties of other materials. Formaldehyde emission from some UF bonded wood products has been recognized for a number of years as a potential source of problem which constitutes a potential health hazard [1]. Supporting the efforts to minimize emission of formaldehyde from resins due to modification [2], the hydrolytic stability of nano-silica based UF composites, UF composites with wood flour (*Pinus silvestris* L.) as natural filler and their hybrid composite were investigated. The hydrolytic stability of UF resins was determined by measuring the mass loss and liberated formaldehyde concentration of modified UF resins after acid hydrolysis [3]. In order to more improve hydrolytic stability, the studied composites have been irradiated (50 kGy) and effect of γ –irradiation was evaluated on the basis of percentage of liberated formaldehyde before and after irradiation. After irradiation, the amount lowering of free and liberated formaldehyde was found (**Fig. 1**). The minimum percentage (1.23 %) of liberated formaldehyde (**Fig. 1**) and mass loss of a 25.35% (**Fig. 2**) were obtained in wood flour bio-modified UF resin after γ –irradiation which indicate significant improvement in the hydrolytic stability compare to other modified UF resins.

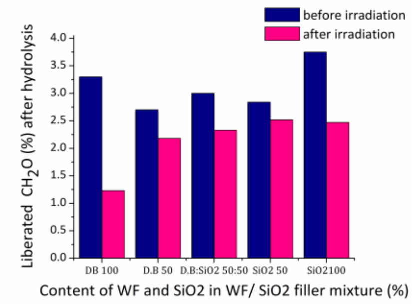

Figure 1. *Percentage of liberated formaldehyde from bio/inorganic modified UF resins*

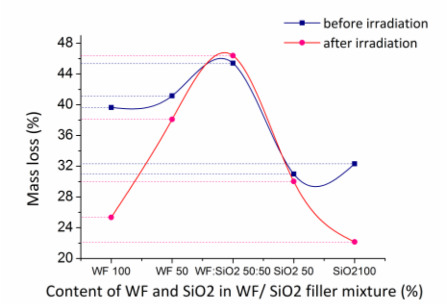

Figure 2. *Percentage of mass loss from bio/inorganic modified UF resins*

Acknowledgement: *Financial support for this study was granted by the Ministry of Educations, Science and Technological Development of the Republic of Serbia (Projects Numbers 45022 and 45020).*

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BS-MC P24

Atypical thermal relaxation of 2 4-substitutes azo-derivatives. Thermodynamic parameters

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The “molecular photo-switching” of the azobenzene type molecules, between the stable *trans* (E) configuration and the *meta*-stable *cis* (Z) form, is an attractive tool that enables fine-tuning of the optical response for polymer materials that incorporate them, to be used as: holographic materials[1], optical storage media[2]. Considerable research has gone into elongating the *cis* lifetime, with the goal of creating bistable photoswitchable systems[3]. Slow thermal back-isomerising azoderivatives are valuable photoactive basic materials for information storage (memory) purposes[4]. A molecular-level memory should be stable and easy to write, and its switched form should be stable but readily erasable when necessary. Consequently, it is essential to have a two-state system that returns to the thermodynamically stable *trans* form in the dark very slow, or maintains in the *cis* form indefinitely. Therefore, finding new azoderivatives exhibiting low isomerisation rates at room temperature is a challenging point of research, consequently one of the main topics of the present work.

Understanding the relationship between particular molecular structures and photo-responsive behaviour represents another important issue in order to gain control over the response time. With this purpose in mind, six different types of hydroxy-substituted azobenzenes were designed and then altered to azo-monomers structures and confronted to their azo-polymers counterparts. Herein, we report the *thermodynamic parameters* determined for 2,4-nitro/cyan substituted azo-derivatives, carried out through UV-Vis spectroscopy. The thermally stable *cis* isomers yielded in our azobenzene derivatives are discussed in terms of geometric considerations and solvent-solute interactions.

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BS-MC P25

FTIR characterization of pectin modified with dicarboxylic acids

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Pectin is a complex polysaccharide consisting mainly of esterified D-galacturonic acid residues in an alpha-(1-4) chain. The acid groups along the chain are largely esterifed with methoxy groups in the natural product. This study presents a new approach for synthesis of modified pectin by introducing crosslinks into a polymer chain. In this manner physical properties such as crystallinity, melting point, glass transition temperature and solubility would be affected. These physical properties would also affect the biodegradability of polymers. The mechanical properties such as tensile strength, impact strength and modulus of polymers would be enhanced by the crosslinking, which is very important in environmental applications as well as biomedical applications. Furthermore, cross-linked polymers have potential for a wide range of applications including biodegradable elastomers, hydrogels and adhesives [1].

This paper reports pectin crosslinking by introduction of ester bonds between free hydroxyl groups of pectin and carboxylic groups of applied acids. Esterification of pectin was carried out in ethanol at 70˚C, using sulfuric acid as a catalyst. As a results of these synthesis pectin esters of adipic, phthalic, oxalic and malonic acids were obtained. After cross-linking treatment new band at 1741 cm^{-1} confirmed ester structure [2]. Depending on diacid that was used yields of the obtained products were compared. Homogeneity of the material was determined using optical microscopy.

The authors acknowledge funding from the Ministry of Education, Science and Technological Development of the Republic of Serbia, Science Project No. 172062.

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BS-MC P26

Degradation of polystyrene-graft-starch copolymers in three different types of soil

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Polystyrene-graft-starch copolymers obtained in the presence of different amine activators (N,N-dimethylethanolamine, N,N-diethylethanolamine, triethylamine, propylamine, iso-butylamine, hexylamine, and 4-(2-hidroxyethyl) morpholine) were subjected to degradation in three different types of commercially available soils (soil rich in humus, soil for cactus and soil for orchid growing), the where percentage of degradation was monitored by mass decrease. During 6 months the amount of degraded copolymer ranged between 12.02 and 57.20 % (in soil rich in humus), 51.54 and 81.30 % (soil for cactus growing) and 10.23 and 63.39 % (soil for orchid growing), clearly showing that the nature of environment and present microorganism community influences the final level of degradation of degradable portion of polymer. There is a significant negative correlation between the share of polystyrene in copolymer and degree of degradation in all three types of soil, while statistical analysis also proved that microorganisms in different soil samples have different degradation capabilities. Grafting of polystyrene on starch on one hand prevents complete degradation of starch that is present (with maximum percentage of degraded starch ranging from 55 to 93 %), while on the other hand there is an upper limit of polystyrene in the copolymer (ranging from 37 to 77 %) above which the biodegradation of degradable part of copolymers is blocked. The reason that degradation is limited is probably due to the fact that in such copolymer, starch is completely covered by polystyrene, and thus non-degradable, while where starch is only partially covered, can be partially degraded, depending of the capabilities of microorganisms present in different soil systems.

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BS-MC P27

Optical and structural characterization of silver/polystyrene nanocomposites by *in-situ* bulk radical polimerization

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Nanocomposites (NCs) with different amount of silver nanoparticles (Ag NPs) embedded in polystyrene (PS) matrix were prepared by *in situ* radical polymerization. In order to achieve homogeneous distribution of Ag NPs in the PS matrix, the nearly monodisperse Ag NPs (7.0 ± 1.5 nm) protected with oleylamine were first synthesized via organic solvo-thermal method and further used as a filler. For this purpose, a simple colloidal method for preparation of Ag NPs in organic solvent was developed. PS was selected as the polymer matrix based on its optical transparency and high chemical resistance. The gel permeation chromatography (GPC) measurements showed that the presence of Ag NPs stabilized with oleylamine during the polymerization of styrene have no influence on the molecular weight and polydispersity of the PS matrix. The structural properties of the resulting Ag/PS NCs were characterized by transmission electron microscope and FTIR spectroscopy. The influence of the presence of Ag NPs and their concentration on the optical properties of PS matrix was investigated in details using UV-Vis spectroscopy. Since the PS represents a nonabsorbing medium throughout the visible spectrum, the improvement of the optical performances of polymer was achieved by incorporation of the appropriate size Ag NPs with strong plasma resonance absorption.

BS-MC P28

Factors influencing steady-state water vapor transfer through clothing materials

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Water vapor permeability is a critical parameter in textile fabric comfort evaluation as it represents the ability of the fabric to transfer perspiration coming out of the human body. Clothing materials with high water vapor permeability allow the human body to take advantage of its ability to provide cooling due to sweat production and evaporation. The influence of several factors such as fabric structure, thickness, porosity and fiber type on water vapor permeability of common clothing materials has been observed by previous researchers. The aim of this research is to investigate the factors influencing steady-state water vapor transfer at the three scale levels of a fabric, i.e. microscopic (fiber type), mesoscopic (yarn structure) and macroscopic (fabric porosity) levels.

Plain knitted fabrics were produced from the two-assembled hemp, cotton and viscose yarns under controlled conditions so as to be comparable in basic construction characteristics. In addition to the structural characteristics of the yarns and knitted fabrics, water vapor permeability and air permeability of the knitted fabrics were measured by standard testing devices (Permetest and TexTest, respectively). The results of air permeability indicated the differences among knitted fabrics coming from the various air volume distributions within the fabrics. As a consequence of the geometry and deformation behavior of the fibers used and spinning technique applied, the yarns differed in both packing density and surface geometry, thus determining the character of the knits' porosity.

The knitted fabrics exhibited the high capability of water vapor transfer as a result of the interlined hollow cavities of cellulosic fibers, as well as the hydrophilic nature of surface of cellulosic fibers which improves adsorption and migration of water vapor along the fiber surface. However, the knitted fabrics were characterized by different water vapor permeability. The viscose knit exhibited the highest water vapor permeability, followed by hemp and cotton knits. Water vapor permeability of the blended knitted fabrics was between the homogeneous counterparts. Bearing in mind the fact that the vapor diffusion through the inter-yarn pores (macropores) within the fabric is far faster than diffusion through the fiber due to lower moisture diffusivity of textile fibers, the analogy between air permeability and water vapor permeability was expected. However, the higher water vapor permeability of the viscose knit in relation to the hemp knit which was characterized by the highest macroporosity, indicated the viscose yarn hairiness as dominant factor of water vapor transfer. In conclusion, the complex impact of variables at the three scale levels of a knitted fabric on its water vapor permeability seems to be confirmed.

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BS-MC P29

Quality of 3D woven sandwich structures in terms of their strength properties

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For a certain period of time textiles with 3D shapes are increasingly used for technical applications. In some areas, 3D sandwich structures play an essential role. Sandwich structure manufactured from a 3D woven fabric consisting of two face fabrics (deck-layers) interconnected by pile yarns is known as Distance Fabric. The space between deck-layers can be filled up with various types of foams forming the sandwich assembly of the specific height. 3D sandwich composites have been widely used in various industrial domains where there was a need for high strength materials [1].

Since 3D sandwich composites have to withstand various heavy loads during application, it is of great importance to examine not only their strength properties but also the strength properties of the Distance Fabric. Based on the results of such investigation, it would be possible to produce Distance Fabric which provides good physical properties of the composite.

The aim of this work was to investigate breaking, tear and puncture strength as well as the corresponding elongations of 3D woven sandwich structure manufactured from Distance Fabric alone. Values of examined strength properties served for establishing dimensionless indicator of quality of observed 3D structures. The experiment was conducted using Parabeam® 3D Glass Fabrics woven out of a 100% E-glass yarn with the spacing of 3 mm and 5 mm between the face fabrics.

The tensile characteristics of fabrics were determined according to the standard method [ISO 13934-1] as well as the puncture characteristics [ISO 12236]. Tear strength and elongation were determined according to the method described in the literature [2].

Imposed investigations showed that breaking strength and tear strength of both Parabeam® 3D Glass Fabrics are greater in warp than in weft direction. Results of breaking, tear and puncture strength tests pointed to the fact that 3D fabric of 3 mm thickness has greater strength but less elongation in relation to the fabric of 5 mm thickness. Based on the values of dimensionless indicator of quality it is possible to conclude that Distance Fabric of 3 mm thickness has better quality in regard to the other investigated Distance Fabric.

Acknowledgements: *The authors are grateful to Ms. Ágota Velkei (Parabeam B.V.) and Mr. Vladimir Dojcilovic (Fluks Trade) for providing Parabeam® 3D Glass Fabrics for this investigation.*

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BS-MC P30

The determination of the antifungal effect of natural extracts with applications in bioremediation

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Biodeterioration of the artefacts can lead to irreparable damages. Biodeteriogens (the biological agents that produce deterioration) [1], can range from microorganisms (as fungi) to higher plants and even animals (some insects, rodents). The most encountered species of biodeteriogens are the fungal species (*Aspergillus Sp., Penicillium Sp., Mucor Sp.*) [2, 3]. The literature data can provide important information about the use of natural extracts as fungicides and thus most of the side-effects of chemical fungicides can be avoided [4, 5]. The present paper describes the methods involved in the determination of antifungal effect of some Romanian native plants (*Allium ursinum*, *Paeonia peregrina var. romanica*, *Lavandula angustifolia*, *Calendula officinalis* and *Ocimum basilicum*). The natural extracts were hydroalcoholic extracts (obtained by two methods) and water extracts. The antifungal effect was determined using two methods: the technique of the diluted inoculums on the surface of the culture media and a modified Kirby-Bauer method [6].

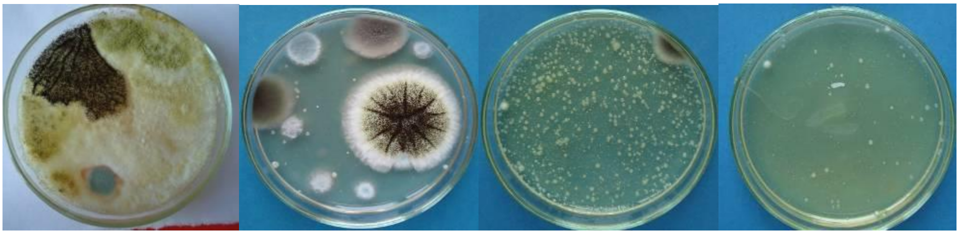

Figure 1. Results obtained using the technique of the diluted inoculums on the surface of the culture media (from left to right – blank sample, treated water Allium ursinum extract, treated hydroalcoholic Allium ursinum extract 1 with SrCaHAP, treated with hydroalcoholic Allium ursinum extract 2)

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BS-MC P31

Evaluation of antifungal effect of synthesized nano and micro materials for applications in cultural heritage conservation

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The methods currently used in bioremediation (gamma or UV irradiation, a series of biocides , etc.) presents several disadvantages (potential harmful side-effects of chemicals on the environment and human health, as well as on the treated artefacts) [1, 2]. Therefore, the development of new bioremediation recipes with low or absent toxicity for humans and to the rest of the environment is of the main importance.

Lin e al. [3] presented the antibacterial effect of partially and totally strontium substituted hydroxyapatite. Starting from this, our group previously presented [4, 5] the synthesis and characterization of new nano and micro-materials that could find applications in the area of cultural heritage. The selected materials could be divided in to two main groups: hydroxyapatite (HAP) and its derivatives (strontium half and totally substituted hydroxyapatite – SrCaHAP, respectively SrHAP, magnesium half and totally substituted hydroxyapatite – MgCaHAP, respectively MgHAP, and barium totally substituted hydroxyapatite – BaHAP) and alkali-earth metal hydroxides ($Sr(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$). The present paper describes the evaluation of antifungal effect of those synthesized materials, performed by two methods: using the technique of the diluted inoculums on the surface of the culture media and a modified Kirby-Bauer method [6].

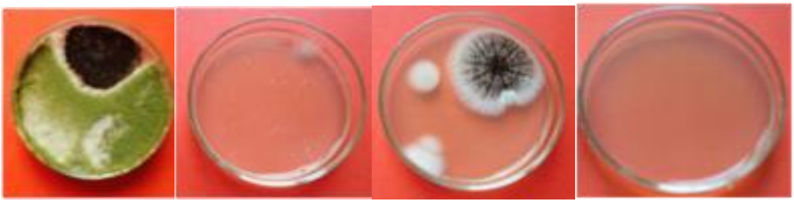

Figure 1. Results obtained using the technique of the diluted inoculums on the surface of the culture media (from left to right – blank sample, treated with HAP, treated with SrCaHAP, treated with SrHAP)

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BS-MC P32

Octadecylsilane-modified mesoporous silica particles doped with olive oil

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It is well known that silica-based hybrids in which organic groups are covalently attached to siloxane networks can be produced by hydrolysis and polycondensation of organosilanes containing Si-C and Si-OR (or Si-Cl) bonds. The chemical design of organosilanes at the molecular scale leads to modifications of the structures and improving of hybrid's properties [1]. Precursors of trialkoxysilanes and tetraalkoxysilanes are usually used for the preparation of hybrid materials, where one organofunctionalized trialkoxysilanes (as the organic functional groups providers) are mixed with tetraalkoxysilanes, (e.g. tetramethoxysilane, TMOS or tetraethoxysilane, TEOS) [2]. The alkoxy moieties undergo hydrolysis and condensation to form the hybrid silica matrix with the organic functionalities covalently incorporated.

In the present work, novel mesoporous silica particles were prepared in aqueous medium by a base catalyzed sol-gel route, using octadecyltrimethoxy silane (ODTEOS) and tetraethylortho silicate (TEOS) as silica precursors. Assessing the influence of the reaction parameters (reaction temperature, reaction time, precursor's ratio and concentration of surfactant) on the physico-chemical properties of the resulted particles is the main go of this work. The pristine or oil-doped ODTEOS/TEOS silica particles were characterized by N_2 adsorption-desorption (porosimetry), dynamic light scattering (DLS), solid-state ^{13}C and ^{29}Si cross-polarization magic-angle spinning nuclear magnetic resonance (CP-MAS NMR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), thermal analysis/ differential thermal gravimetry (TGA/DTG) and infrared spectroscopy (FTIR). The results showed that the particles average diameter depends strongly of the molar ratios of silica precursors and of surfactant or oil presence in the reaction system. Variation of the silica co-precursor type and the presence of the surfactant in the sol-gel system also induced morphology transformation. ^{13}C CP/MAS NMR spectra revealed the higher mobility of $(CH2)_n$ group (from the long alkyl chains of the surfactant and of the hydrolyzed ODTEOS) in the silica hybrid material, when the oil molecules were present in the sol-gel system. The presence of oil in the sol-gel reaction mixture also had a visible effect on the inner structure of the mesoporous silica, narrowing or broadening the pore size distribution and decreasing or increasing the mean pore diameter.

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BS-MC P33

Poly(ε-caprolactone)-poly(ethylene oxide)-poly(ε-caprolactone): biodegradable triblock copolymer as a matrix for controlled drug release

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Aliphatic polyesters have been recognized as one of the most promising biodegradable materials because they are readily susceptible to biological attack. The biodegradable properties of polyesters can be improved by increasing the hydrophilicity through the introduction of hydrophilic segments, such as polyethers, into the polymer chains. Poly(ε-caprolactone), PCL, semi-crystalline and hydrophobic polymer with slow degradation rate, has received much attention as a polymeric matrix for drug delivery applications. Hydrophilic poly(ethylene oxide), PEO, can be selected to be attached to PCL, due to its hydrophilic, non-toxic and antigenic or immunogenic properties. PCL-PEO amphiphilic copolymers exhibit higher biodegradability, higher hydrophilicity and better performance in biomedical applications than PCL homopolymer [1].

Two series of triblock copolymers, which consist of poly(ethylene oxide) as a central block and poly(ε-caprolactone) as lateral blocks were synthesized by a ring opening polymerization of ε-caprolactone in the bulk. The synthesis of ε-caprolactone were initiated with the terminal hydroxyl functional groups of PEO of two different molecular weights (400 and 1000 g/mol) and tin(II) 2-ethylhexanoate was used as a catalyst. The copolymers with different PCL block lenghts and weight fraction ranging from 95 to 99 wt.% were synthesized by adjusting the molar ratio of the reaction mixture. The composition and structure of these copolymers were determined by ^{1}H NMR spectroscopy. The molecular weights of the polyesters were evaluated from solution viscosity measurements and by gel permeation chromatography (GPC). The thermal properties were investigated using differential scanning calorimetry (DSC). The degree of crystallinity was determined by means of DSC and wide-angle X-ray scattering. In order to evaluate the degree of hydrophobicity and wettability of the PCL-PEO-PCL, static water contact angles were measured. The surface morphology of copolyester films was investigated by SEM and optical microscopy. The properties and behavior of synthesized copolymers were compared to PCL homopolymer. The synthesized copolyesters were evaluated for use as a polymer matrix in the preparation of micro- or nano- spheres in controlled drug delivery systems.

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BS-MC P34

Influence of chemical composition on the strength characteristics of hot rolled steel sheets

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This paper deals with the influence of content of carbon, manganese and vanadium in the steel on the mechanical properties of steel sheets in the hot rolling process [1,2].

Three diffetent types of steels were analyzed: non-alloy structural steels, steels for boilers and pressure vessels and heat-resistant pressure-vessel steels [3-5]. The content of C, Mn and V in the steels varies to 0.17 %, 1.45 % and 0.065 %, respectively. The parameters of hot rolling processes and geometrical parameters of the steel sheets were followed after each rolling pass.

The influence of the chemical composition of the steels and the reduction degree on their mechanical properties was determined. It was shown that with the increase of the content of C and Mn in the steel, the strength characteristics of the sheets are increasing from 5.4 % to 9.2 % and the elongation is decreasing to 4 %. The toughness of the sheets is increasing with the increase of the content of Mn, for 12.7 %, and V, for 68 %, and with the decrease of content of C for 8.8 %.

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BS-MC P35

Swelling Characterization and Adsorption Properties of Magnetic Hydrogels

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Introduction

Crosslinked polymers are capable of swelling up to a hundred times, in some cases even thousands of times, more than their dry mass in aqueous environments by imbibing large amounts of water due to the hydrophilic groups (-OH, -COOH, $-NH_2$, $-CONH_2$, $-SO_3H$) in their polymeric networks. These unique properties give hydrogels many advantages for their use in applications as broad as bioengineering, pharmaceuticals, medicine, food industry, water purification, sensors and so on. There are many investigations into the removal of toxic metal ions and dye molecules by hydrogels [1,2].

Experimental

In this study, crosslinked polymers were synthesized using of acrylamide (AAm) and 2-akrilamido 2-methyl propane sulfonic acid (AMPS). Hydrogels were prepared by free radikal polymerization in aqueous solution using poly(ethylene glycol)diacrylate (PEGDA) as crosslinkers. For the preparation of magnetic hydrogels the synthesized hydrogels were loaded with iron (Fe^{2+}, Fe^{3+}) ions. After loading process iron ions were reduced by using amonium hydroxide [3]. Structural characterization of chemicaly crosslinked polymers was made by Fourier Transform Infrared Spectroscopy (FT-IR) analysis. Scanning electron microscopy (SEM) images were taken for determination of surface porosity of hydrogels. Dynamic swelling tests were applied at 25°C for the purpose of investigation of swelling properties of crosslinked copolymers. According to obtained data, parameters concerning swelling kinetics and diffusion mechanism were calculated. For the aim of investigation of adsorption properties of crosslinked copolymers, Janus green B was chosen as a model molecule [4].

Conclusions

The equilibrium percentage swelling ranges are 1530-3500% for AAm/AMPS hydrogels and 1165-3095% for Mag-AAm/AMPS magnetic hydrogels. Equilibrium swelling of hydrogels increased with the increasing of AMPS content. At the end of the sorption study AAm/AMPS and Mag-AAm/AMPS hydrogels showed the high sorption capacity for Janus green B.

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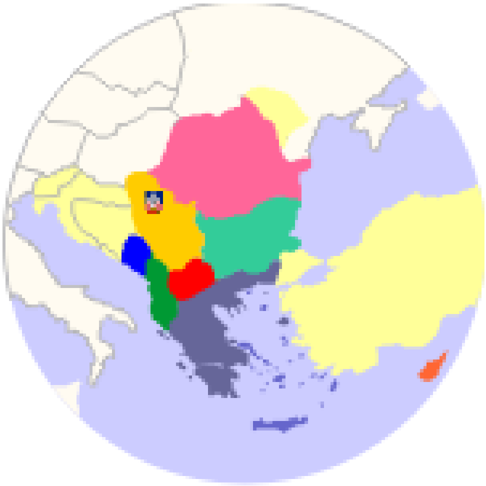

Supramolecular Chemistry

BS-SC P01

New inorganic-organic composites with enhanced thermal and mechanical properties

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In the last decades polymer composites have received attention due to possibility of obtaining materials with improved thermal [1,2] and mechanical [3,4] properties compared to the pure polymer. A microporous synthetic zeolite, HZSM-5, was used as inorganic structure in order to obtain new host-guest hybrid composites in ultrasonic field. The use of polyvinyl acetate within an inorganic matrix improves the physical properties and modifies the thermal and mechanical properties of the obtained materials. The molecular weights were determined by Gel permeation chromatography (GPC), the thermal transitions were assessed by thermal gravimetric analysis (TGA), derivative thermogravimetry (DTG) and dynamic mechanical analysis (DMA) and also the morphology was pointed out by scanning electron microscopy (SEM). The performed investigation shows that the vinyl acetate has been successfully used to enhance the thermal and mechanical performance of synthesized hybrid composites.

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BS-SC P02

Imprinted mesoporous molecular sieve MCM-48 for gallic acid separation

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Modern separation techniques use adsorbents with high advanced porous surface, high values of static adsorption capacity, selective properties and stability in aggressive environments [1]. Depending on the concentration of the surfactant added in the synthesis and temperature, hydrolyzed silicone alkoxides reorganise to form micelles in hexagonal ordered arrays (MCM-41), cubic ordered arrays (MCM-48) or lamellar ordered arrays (MCM-50), leading to various nanostructured materials [2]. The methodology for the preparation of cubic mesoporous molecular sieves MCM-48 was approached to produce molecularly imprinted polymers (MIP) using gallic acid (GA) as template. The simplified mechanism for molecularly imprinting with GA is presented in **Figure 1**. The stability of imprinted cavities was given by the sol-gel process, using tetraethoxysilane (TEOS) and vinyltriethoxisilane (VTEOS) followed by copolymerisation of vinyl functionalities of VTEOS with those of styrene trimethyammonium chloride (STMACl). STMACl plays a double function: as stabiliser for the micelles and as functional co-monomer for the final polymerization process. MIP properties were compared to those of a blank polymer (NIP) synthesized in the same conditions as the imprinted one but without GA. The infrared (FTIR) spectrum of MIP before GA extraction presented dissimilarities compared to the one recorded after GA extraction and with that of NIP, suggesting the existence of particular GA-Polymer substrate interactions. Adsorption-desorption kinetics of GA from ethanol and selectivity were in agreement with the morphological (SEM, DLS) and thermal proprieties (TGA).

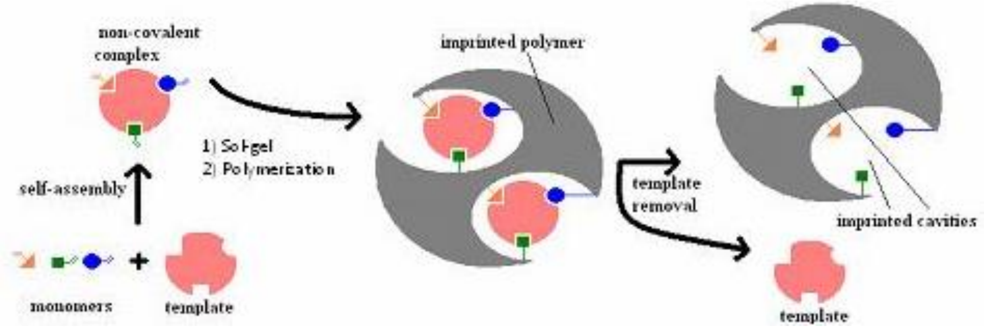

Figure 1 A simplified mechanism of molecularly imprinting: (1) first step sol-gel using TEOS/VTEOS and STMACl as monomers and stabiliser, respectively; (2) second step polymerization of vinyl functionalities of VTEOS and STMACl

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BS-SC P03

Physico-chemical properties of Triton X-100 - Tween mixed micelles

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Knowledge of physico-chemical properties of mixed micelles is important in order to design drug carriers having improved properties. In this work, physico-chemical characteristics of binary mixed micelles of Triton X-100 and homologous series of four Tween amphiphiles (Tween 20, Tween 60, Tween 80 and Tween 85) were investigated and analysed in the viewpoint of the regular solution theory. One of the most important aims of this study was to investigate how variations in side chain of Tween molecules influence on the interactions with Triton X-100.

The critical micelle concentration (cmc) values were determined using spectrofluorimetric measurements. The results show synergistic behaviour between Triton X-100 and Tween 20, 60 and 85, while in Triton X-100 and Tween 80 mixtures, antagonism was detected.

Based on the calculated values of the β parameter, the strongest synergistic interactions were noticed between Triton X-100 and Tween 60.

This is most probably due to the difference in conformational rigidity of the hydrophobic chains of the investigated Tweens. Namely, longer and unsaturated lateral sides have greater conformational freedom, thus forming hydrophobic phase easier. Therefore, Tween 60 having stearic residue (C18) shows stronger interactions than Tween 20 consisting of laurate alkyl tail (C12), while Tween 80 shows antagonism because its oleate chain has rigid cis configuration due to the C9 double bond.

However, Tween 85 consisting of three oleate alkyl tails shows stronger attractive interactions with Triton X-100 than Tween 80, most probably since these oleic residues group together to form the hydrophobic cage which packs more easily in the hydrophobic domain than single unsaturated tails.

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BS-SC P04

Determination of the aggregation numbers of bile salts micelles

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The special geometry of the steroid skeleton causes that bile acids anions, in contrast to aliphatic amphiphiles, form micelles with a small aggregation number [1]. In view of the tendency to reduce membrane toxicity, pharmacological investigations of bile acids are mainly concerned with their oxo derivatives [2]. Since micelles of these bile acids have been insufficiently studied, the objective of this work is determination of aggregation numbers of corresponding micelles monomers. The aggregation numbers were determined based on the freezing point depression of the solutions by applying the appropriate equations of Debye-Hückel, Guggenheim and Gibbs-Duhems, and using pNa data measured with the aid of a Na-selective electrode. Depending on the structure of the bile acid anion, the values obtained for the aggregation numbers were in the range from 2.09 to 3.44. The increase in the number of oxo groups in the molecule is accompanied by a decrease in the hydrophobicity of the convex side of the steroid skeleton of the bile acid anion, resulting thus in a lower aggregation number. Obtained results indicate that C12 and C7 α-axial OH groups and oxo groups at the same C atoms of the investigated bile acid molecules have a different spatial environment.

The work was financially supported by the Provincial Secretariat for Science and Technological Development, AP Vojvodina, Republic of Serbia, Grant No. 114-451-2113/2013. The Ministry of Science and Technological Development of the Republic of Serbia (Project No. 172021) is acknowledged as well.

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BS-SC P05

Synthesis and characterization of polymer-silica hybrid latexes obtained by emulsion polymerization and sol-gel process for ultra-hydrophobic coatings

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Preparation of polymer/silica hybrid materials through in situ emulsion polymerization and sol–gel process, using organic monomers and inorganic precursors, were employed in a variety of application fields, such as coatings, optoelectronic devices, sensors, etc. [1, 2].

In the present work, polymer-silica hybrid latexes based on methyl methacrylate (MMA), butyl acrylate (BuA), 2-hydroxyethyl methacrylate (HEMA), and different inorganic precursors (tetraethoxysilane (TEOS), methyltriethoxysilane (MTES), isobutyltriethoxysilane (IBTES), diethoxydimethylsilane (DEDMS), vinyltriethoxysilane (VTES)) were synthesized by emulsion polymerization and sol-gel process. The resulting latexes were characterized both as materials placed into plastic vials and as films deposited onto clean glass slides by various techniques including Fourier transform infrared (FT-IR), UV–vis spectrometry, environmental scanning electron microscopy (ESEM), thermal analysis (TGA) and water contact angles of film surfaces. The results showed that the surface wettability was changed from hydrophilic to hydrophobic by adding a precursor with hydrophobic organic group. For all hybrid latexes, the Si-O-Si groups give a strong absorption band in the spectral region between 1250-1000 cm^{-1} (asymmetric stretching vibration), which confirms the formation of a network structure inside the films. The antireflective films, due to diffuse reflection, have been given by the preparation from inorganic precursors.

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BS-SC P06

Micellar properties of salts of naphthenic acid mixtures

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The critical micelle concentration (cmc) values of surfactants are important in many fields of industrial applications, where solubilization, emulsification or suspension stabilization is required. Another application of the determination of the cmc values is investigation of micellar properties of amphiphiles.

In this work, the cmc values of three different fractions of salts of naphthenic acids from Velebit oil source were investigated at seven different temperatures ranging from 10 to 40°C. The critical micelle concentration (cmc) values were determined using spectrofluorimetric measurements. The fractions of naphthenic acids were acquired at three different pH values (4, 8 and 10). The fraction attained at pH 4 is composed of tricyclic naphthenic acids, while the portion acquired at pH 8 consists of bicyclic and tricyclic naphthenic acids predominantly. The pH 10 fraction consists of aliphatic naphthenic acids mainly.

Based on the determined cmc values it can be concluded that fractions having tricyclic and/or bicyclic salts of naphthenic acids have larger cmc values, most probably due to the greater rigidity of these structures which makes them difficult to pack in the hydrophobic micellar domain. Therefore, the micelles of these salts of naphthenic acids are less flexible and more exposed to water molecules causing the decrease in lipophilicity of micellar region. Also, the increase in the cmc values was observed with the increase in temperature for all fractions, that represents common characteristic of ionic amphiphiles.

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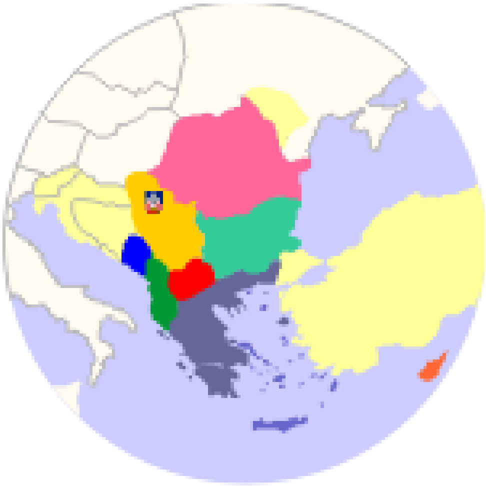

Nanoscience

O 22 BS-NS

Amsacrine-loaded mesoporous silica-based nanoparticles for visible light responsive anticancer treatment

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Construction of stimuli-responsive drug delivery systems (DDSs) has been an attractive research field in recent years due to possible application for selective anticancer treatment. Mesoporous silica nanoparticles (MSNs) are particularly attractive scaffolds for construction of such drug delivery nanodevices due to high surface area, isostructural mesoporosity and a particle diameter (100–200 nm) in the range needed to enhance the targeting ability of a DDS through the enhanced permeability and retention (EPR) effect of cancerous tissue. Drugs can be loaded inside the mesoporous framework and entrapped by the addition of various mesopore capping agents. Cargo molecules are then released only upon exposure to stimuli, which induce the removal of capping moieties and facilitate the control over delivery process.

We previously developed MSN-based supramolecular assembly for visible light induced controlled release of cargo molecules.[1] Sulforhodamine 101 was loaded inside the mesopores of mercaptopropyl- functionalized MSN and the cargo molecules were entrapped by the presence of $Ru(bpy)_2(PPh_3)$-moieties, coordinated to mercaptopropyl functional groups. Upon irradiation with visible light Ru–S coordination bond is cleaved, which triggers the release of capping species and loaded molecules.

Herein we are reporting a study on capability of $[-Ru(bpy)_2(PPh_3)]$ moiety to entrap anticancer drug amsacrine (AMS) inside the mesopores of MSN, and the applicability of the as-constructed nanodevice to deliver AMS to cancer cells by visible light irradiation.

The release kinetics of AMS and capping moieties from the constructed material AMS@[Ru]-MP-MSN is measured by fluorescence and absorption spectroscopy respectively, while the material is characterized by nitrogen adsorption/desorption measurements, TEM and EDS spectroscopy.

Applicability of the constructed nanodevice for visible light-responsive anticancer treatment was demonstrated by measuring viability of AMS@[Ru]-MP-MSN-treated HeLa cell cultures, which were exposed to irradiation from royal blue LED lamp (peak wavelength at 447.5 nm).

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O 23 BS-NS

Characterization of nanocapsules containing *Elaeagnus angustifolia* L. extract prepared using an emulsion-diffusion process

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Nanocapsules loaded with bioactive compounds derived from medicinal plants have numerous possibilities in the development of biochemical delivery systems. *Elaeagnus angustifolia* L., commonly known as Russian olive, has traditional medicinal use in the Middle East as an analgesic for arthritis and joint pain. Because *E. angustifolia* contains vitamin A, vitamin B, abundant calcium, and vitamin [illegible] an effective coagulant, it has been considered as potentially beneficial in wound healing and scar formation, as well as treatment or prevention of osteoporosis. Nanocapsules containing an *E. angustifolia*-filled core can be fabricated employing polymerization. In this process, nanocapsules are prepared using poly ethylene glycol-poly butylene adipate-poly ethylene glycol (PEG-PBA-PEG) as a shell surrounding a core of *E. angustifolia* and olive oil. In this study, relative proportions of polymer and oil, concentrations of polymer and bioactive compound, and presence or absence of various surfactants in different concentrations were investigated in relation to the particle size of the final product. A comparison of samples obtained using the surfactants Tween 80, Tween 60, poly vinyl alcohol (PVA), mixed Tween 80 and PVA, and mixed Tween 80 and Tween 60 showed Tween 80 to result in the smallest particle size. An oil-to-polymer ratio of 1:0.25 resulted in the smallest nanoparticle size. Smaller nanoparticles sizes were obtained using lower concentrations of polymer and higher concentrations of the bioactive compound. Fourier transform infrared spectroscopy (FTIR), hydrogen-1 nuclear magnetic resonance (^{1}H NMR), particle size analysis (PSA) and scanning electron microscopy (SEM) were used to identify and characterize the nanocapsules.

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O 29 BS-NS

Mesoporous silica nanoparticle-based drug delivery systems for stimuli responsive drug delivery

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Construction of functional supramolecular nanoassemblies has attracted great deal of attention in recent years for their wide spectrum of practical applications. Mesoporous silica nanoparticles (MSN) in particular were shown to be effective scaffolds for the construction of drug carriers, sensors and catalysts. This lecture overviews construction and characterization of stimuli-responsive controlled release MSN-based assemblies for drug delivery. UV light responsive delivery of doxorubicin, a widely used anticancer drug, is successfully demonstrated from nitroveratryl carbamate protected aminopropyl-functionalized MSN. [1] The drug delivery principle is based on charge repulsion between UV light-generated positively charged propylammonium ions and positively charged doxorubicin molecules. Release of the drug also increases by lowering pH value from 7.4 to 6.4. This result is beneficial for selective drug delivery to tumor tissues, as most tumor tissues have low extracellular pH value.

A supramolecular assembly for visible light responsive release of cargo molecules is also demonstrated.[2] Sulforhodamine 101 was loaded inside the mesopores of mercaptopropyl-functionalized MSN and entrapped by mercaptopropyl- coordinated $Ru(bpy)_2(PPh_3)$-moieties (bpy = bipyridine, PPh_3 = triphenylphosphine). Irradiation with visible light triggers the release of capping species and loaded molecules.

A series of core/shell, iron oxide nanoparticle embedded magnetic mesoporous silica nanoparticle materials with radial and hexagonal porous structures are synthesized and their capacity to load and release the anticancer drugs, 9-aminoacridine and camptothecin are demonstrated.[3] The results indicated that release of 9-aminoacridine is hindered, meanwhile the loading and release of camptothecin was promoted by the presence of organic functionalization bound to the pore surface. The cell viability assay on Chinese hamster ovarian cells supported the drug release results and showcased the capability of organic functionalization to govern the anticancer activity of drugs. The application of magnetic field to control the rate of drug release from magnetic drug-delivery carriers was also demonstrated, which may open possibilities for *in vivo* targeted delivery of drugs by an externally applied magnetic field.

Magnetic mesoporous silica nanoparticles-based photosensitive drug carrier for UV light-responsive release of camptothecin was also constructed.[4] Cooperative anticancer effect of mesopore-loaded camptothecin and mesopore-capping CdS nanoparticles was observed under UV irradiation of the material-treated CHO cells, which may help to increase the effectiveness of anticancer treatment by decreasing the possibility of development of resistance to the treatment.

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BS-NS P01

Two-step modification of silica nanoparticles for covalent lipase immobilization

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Lipases are enzymes very well known for their laboratory and industrial application. Various immobilization supports and techniques were examined in order to improve lipase stability and activity for industrial application. Lipase can be immobilized by adsorption, entrapment or by covalent binding [1]. Different supports are considered for enzyme immobilization, organic or inorganic, natural or synthetic, but there is no unique solution. Ideal support should posses enough active groups to interact with enzyme, but to be inert to reaction media; it should be mechanically stable, renewable for many cycles and inexpensive. Lately, nanoparticles of silica are used for enzyme immobilization because of its extremely high surface area and controllable pore size. Nanoparticles of silica are characterized by surface to volume ratio that is significantly higher than commonly used supports. Some of the authors have also presented that nanoparticles of silica have stabilization effect for the immobilized enzyme molecules[2]. Also in some cases immobilization on nanoparticles also provides temperature stability of immobilized enzyme[3].

In this study, nanoparticles of silica were modified in two-step process. The goal was to introduce new reactive groups on silica surface, and make silica surface more suitable for immobilization of lipase. In first step, nanoparticles of silica were treated with (3-aminopropyl)-trimethoxysilane (APTMS), and then in step two, silica particles were treated with cyanuric chloride (CTC) (temperature and molar ratio silica/CTC were variated). This way nanoparticle of silica became rich in chloride groups, which enabled covalent immobilization of lipase. FTIR analysis was performed after each modification step, and confirmed presence of new active groups. Better results were obtained when second step of modification was performed at 0 °C and high molar ratio silica/CTC. Lipase from *Candida rugosa* was immobilized on modified nanoparticles of silica. Amount of proteins bound was in range between 55 and 78%, but activity retention after immobilization process was approximately 30%. Immobilized enzyme was used in reaction of aroma ester synthesis, and reached conversion rate of 30% within 8 h.

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BS-NS P02

Preparation and properties of poly(ε-caprolactone)/organoclay nanocomposites

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In the recent years, biodegradable polymers are attracting intense interest due to growing environmental concerns as well as their potential application in biomedical field. The most prominent class of synthetic biodegradable polymers is biodegradable polyesters (also called biopolyesters), such as poly(lactic acid) or poly(ε-caprolactone). Poly(ε-caprolactone), PCL, is semi-crystalline polyester with low melting (60 °C) and glass transition (-60 °C) temperature. PCL has a great potential in short-life range applications (*e.g.* packaging, agriculture) and as a biomaterial (e.g. tissue engineering, drug delivery)[1], due to its fair mechanical properties, good processability, compatibility with many other polymers and biocompatibility. Wider application of PCL as biodegradable material is hampered by its low stiffness, for applications in load bearing conditions, high permeability to gasses and solvents and poor thermal properties. For the particular applications, performance of biodegradable polyesters can be improved by the incorporation of nano-sized layered-silicates[2]. Such nanocomposites possess better mechanical and barrier properties, reduced flammability, improved thermal stability and higher heat distortion temperature. The most commonly used clay as a nano-sized filler for biodegradable polyesters is montmorillonite, MMT, which belongs to the family of 2:1 layered phyllosilicates. For the improved compatibility with organophylic polymeric matrix, which will result in higher performance of nanocomposite, nano-clays are usually modified by ammonium or phosphonium cations bearing at least one long alkyl chain. The chemical structure of organic modifier is crucial for the compatibility of nano-sized filler with polymer matrix and can also have an influence on melt-processabilty or thermal properties[3].

The aim of this study was to prepare and compare the performance of PCL/organoclay nanocomposites with two different organically modified montmorillonites, OMMTs. The two OMMTs, which were used, are commercial products: Cloisite® 30B and, more hydrophobic, Cloisite® 15A. Nanocomposites with 1, 3, 5 and 8 wt % of OMMTs were prepared by the solvent intercalation procedure from a chlorophorm solution. PCL/OMMT nanocomposites were characterized in terms of morphology and clay dispersion by optical microscopy, SEM and WAXS. The thermal properties and degree of crystallinity were determined by DSC. Thermal stability was investigated in non-isothermal TG experiments. Mechanical properties of different nanocomposites were compared in tensile tests.

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BS-NS P03

Physico-chemical properties of bile salt-Tween 80 and Tween 40 mixed micelles

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In this work mixed micelles [1] of Na salts of bile acids and Tween 80 are studied. In the experiment, number and orientation of OH and oxo groups in the steroid skeleton of bile acid anion varies. In every Na salt of bile acid, mole fraction of Tween 80 (α) varies from 0.05 to 0.5. Critical micelle concentrations of binary surfactant mixtures are determined by tensiometric and conductometric methods (modified Philips method of data processing). By employing regular solution theory for every studied binary surfactant mixture, values of interaction coefficient ($\beta_{1,2}$) are determined. Based on the obtained $\beta_{1,2}$ values, investigated bile salt anions form two groups. Group I consists of bile acids having only OH groups attached to the steroid skeleton. Characteristics of mixed micelles of this group are negative values of $\beta_{1,2}$ for α to 0.1 (synergistic effect between different types of the micelle building units), and positive values of $\beta_{1,2}$ for α over 0.1 (antagonistic effect). This change of sign of $\beta_{1,2}$ as a function of α can be explained by phase transformation in mixed micelle as a pseudo-phase, and due to rigid geometry of cis-oleic residue of Tween 80. Group II is formed of bile acid anions having one or more oxo groups in the steroid skeleton. Mixed micelles of Tween 80 and group II of bile acid anions are characterized by positive $\beta_{1,2}$ values in the whole investigated range of α. Based on the intensity measurements at different temperatures of first (I_1) and third (I_3) vibrational bands of pyrene (probe molecule) emission spectrum as a function of total surfactant concentration, it can be concluded that mixed micelles having Tween 80 are less rigid than mixed micelles having Tween 40. This also indicates that in hydrophobic domain of mixed micelles, cis-oleic residues are more difficult to pack together compared to the palmitic residues of Tween 40 [2].

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BS-NS P04

Preparation and characterization of epoxy resin and alkyl gallates modified TiO_2 nanocomposites

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Epoxy resins are characterized with outstanding performances such as toughness, rigidity, high temperature performance, chemical resistance, adhesive properties, formulation latitude, and reactivity with a wide variety of chemical curing[1].

The purpose of this study was to prepare and investigate the influence of surface modified titanium dioxide nanoparticles to commercial epoxy resin. TiO_2 colloid solution was synthesized by hydrolysis of titanium isopropoxide at 80 ˚C for 8 hours [2]. The surface of TiO_2 nanoparticles was modified with three gallic acid esters (propyl, hexyl, and lauryl gallate). Modification of TiO_2 colloidal particles was performed by dissolving of certain gallate in a mixture of chloroform and methanol and mixing with colloid solution of TiO_2, and separating of dark-red organic phase, containing the surface modified TiO_2 particles, from the aqueous phase [3].

The commercial epoxy resin, CHS 210x75, and curing agent, Epicure 3115x70, were mixed in a weight ratio 3:1. Nano composites based on epoxy resin and TiO_2 nanoparticles were obtained by adding 1 wt% gallate modified nanoparticles to the epoxy/hardener system. Films of uniform thickness were obtained by applying the composite solutions with wire-wound rods at 10x10 cm glass plates and curing them at room temperature for 21 days.

FTIR and UV-Vis spectroscopy were used to confirm the formation of a charge transfer complex between the surface Ti atoms and the gallates.

Mechanical properties of nanoparticles/epoxy polymeric films were also investigated. The Konig pendulum test was used for hardness determination of epoxy films. Adhesion was determinated by cross cut test. Cupping tester was used to measure elongation and deformation of films, and water vapor transfer through epoxy films were measured by permeability testing cups.

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BS-NS P05

Anticorrosive coatings based on epoxy/organoclay nanocomposites

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The mechanical, thermal, barrier and anticorrosive properties of polymer coatings could be significantly improved by incorporation of small quantities of clay nanoparticles into the polymer matrix. It is known that the barrier effect of polymer coatings can be increased in the presence of nanoclay as a consequence of its high aspect ratio (70-150) and large surface area (750 m^2/g) [1]. The extent of exfoliation or intercalation of nanoclay particles in the polymer matrix is crucial for the achievement of higher barrier effect [2].
In this work epoxy/clay nanocomposites (NCs) based on diglycidyl ether of bisphenol A (DGEBA) epoxy resin, polyamidoamine curing agent and 1-10 wt% of commercial organoclay Cloisite 30B were prepared by the solution intercalation method. Further, the epoxy NC-based coatings were prepared using NCs with 1 and 3 wt% clay content with a mainly exfoliated structure in epoxy primer and topcoat, using a standard commercial recipe and procedure. These epoxy NCs and NC-based epoxy primers and topcoats applied on metallic substrates were tested: in „Pull-off“ and Cross-cut adhesive tests, for the mechanical properties such as hardness (Persoz, Konig), elasticity (Erichsen cupping test), flexibility (Erichsen conical mandrel bend test) and impact resistance. It was found that epoxy NCs had reduced adhesive and mechanical properties in comparison to cured epoxy resin, especially elasticity and impact resistance. This is probably due to clay particles located on metal-epoxy NCs interface where they reduced the interactions between metal and epoxy resin and/or heterogeneous structure of the samples [3]. On the other hand, the incorporation of nanoclay in epoxy coatings didn’t significantly change the adhesive and mechanical properties. The hardness, elasticity and impact resistance of primer and impact resistance of topcoat were even slightly improved for NCs with 1 and 1-3 wt% clay, respectively. In order to investigate anticorrosive properties of the two layer coating systems with modified epoxy primers and unmodified topcoat were analyzed in salt spray test. Coating systems based on modified primers after 200 and 500 h had lower amounts of rust and blister density than unmodified coating system. Thus, anticorrosive properties of epoxy coating were improved.

Acknowledgements: This work was partially financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172062).

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BS-NS P06

Dependence on J-aggregate formation on TC and Ag nanoparticles concentration

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In this work we observed a change in the absorption spectrum, depending on the concentration of 3,3’ – disulfopropyl 5,5’ – dichlorothiacyanine (TC) dye and silver nanoparticles (AgNPs). In solution TC dye is present as an equilibrated mixture of monomers and dimers. The absorption spectrum shows two peaks, one at 409nm which is assigned to the dimer and the other one at 428nm is assigned to the monomer [1]. Absorption spectrum of AgNPs contains surface plasmon absorption band resulting from excitation of the electron gas and it is located at 390nm [2]. After mixing Ag colloid and TC solution the new band appeared at 481nm [3]. The intensity of the absorption peak at 481nm depended strongly on AgNPs as well as on TC concentration. The dependence of spectral changes vs. TC or AgNPs concentration enabled us to determine themolar absorptioncoefficient of J-aggregates at 481nm. The absorbance at 481nm was followed as a function of AgNPs concentration, keeping TC concentration constant, and vice versa. The concentration of aggregates was defined in terms of concentration of aggregated monoformic TC dye molecules. The spectrophotometric measurements of J-aggregate formation included both absorption and light scattering and therefore were more appropriately refered to measurements of coefficient. The value for $\varepsilon_{J/monomer}$ 1.08x10^5 M^{-1} dm^3 cm^{-1} was evaluated from the plateau of sigmoid shaped curves as the mean value for the complete conversion of TC molecules into J-aggregates.

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BS-NS P07

Structure, morphological and thermal properties of thermoplastic polyurethane/organically modified montmorillonite nanocomposites

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The aim of this work was to synthesize a new series of thermoplastic polyurethane (TPU) nanocomposites in order to improve thermal, mechanical, barrier and biocompatible properties of TPUs for potential biomedical applications. Nanocomposites with 20 wt. % of hard segments were prepared with addition of organically modified montmorillonite clay (Cloisite 30B) by *in situ* two-step polyaddition reaction in solution. Hard segment of TPU prepared in the form of film, consist of 4,4′-methylenediphenyl diisocyanate and 1,4-butanediol, while α,ω-dihydroxyethoxy propyl poly(dimethylsiloxane) was used as the soft segment. Different content of organoclay (1, 3, 5, 8 and 10 wt. %) was incorporated into TPU matrix in order to examine the influence of the nanoclay content on the structure, morphology and thermal properties. The structure of obtained nanocomposites was confirmed by FTIR spectroscopy. Morphological characterization of nanocomposites was carried out using wide-angle X-ray diffraction (WAXD) and scanning electron microscopy (SEM) techniques. SEM and WAXD results confirmed a well dispersion of intercalateed/exfoliated structure of organoclay nanofillers in the TPU matrix, when the content was up to 5 wt. %. Thermogravimetric analysis (TGA) revealed that incorporation of organoclay particles significantly enhances the thermal stability of nanocomposites in comparison with pure TPU. Differential scanning calorimetry (DSC) was used to determine the melting, crystallization and glass transition temperatures of hard segments, which was found to shift toward higher temperatures upon increasing the organoclay content to 5 wt. %, but then there were no changes when the organoclay content increased to 10 wt. %. The presence of layered silicates from organically modified montmorillonite clay in TPUs can result in more ordered hard segments having higher melting temperature, that in other hand show loss in crystallinity of the hard segments. It is estimated that the total degree of crystallinity of nanocomposites was in the range from 3.1 to 3.9 %, while for pure TPU it was 4.3 %. It can be concluded that the organoclay particles are homogeneously dispersed in TPU matrix with lower content of organoclay and preferentially embedded in the hard segment phase of TPUs.

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BS-NS P08

Natural rubber / organo-montmorillonite nanocomposites: rheometric and mechanical properties

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In rubber compounding fillers are irreplaceable ingredients. Rubber application, demand products with certain strength and at the same time outstanding elastic properties. Both depend on the amount of filler. For the conventional fillers (carbon black and silica used in bulk quantities), the strength of rubber increases but the elasticity decreases with the amount of filler. This conflict could be generally solved by using small quantities of nanofilers [1]. Layered silicates due to their high aspect ratio, arising from their platelet-like morphology are potentional nanofillers for polymers. Montmorillonite is the most applied clay for the preparation of polymer nanocomposites, due to its large availability; low cost and high surface area [2].

The aim of the present work is to evaluate the properties of NR/ quaternary alkylammonium modified montmorilonite (OMMT) nanocomposites in comparison with NR filled with carbon black. Natural rubber/organomodified montmorilonite nanocomposites with different content of OMMT were prepared by melt mechanical mixing on standard equipment (open two-roll mill). The structure of the nanocomposites was characterized by XRD. The vulcanization behaviour and mechanical properties of NR/OMMT vulcanizates were compared with a referent natural rubber compound containing 60 phR carbon black as reinforcing filler. The effects of organoclay and its content on the swelling behaviour of the rubber samples was investigated as well.

XRD analysis indicated that the elastomer chains were intercalated into montmorilonite galleries. Organoclay accelerate the vulcanization reaction decreasing optimum cure time (t_{90}) and scorch time (t_{s2}). Furthermore, it gives rise to a higher crosslink density. Addition of organoclay improves the strength of the natural rubber, even at very low content (2 phR) and at the same time improves the elasticity of the material, which is not the case for carbon black filler. The nanocomposite containing 2 phR OMMT has 29% improved tensile strength and 61% improved elongation at break in comparison with the referent material. The results confirm that standard shear mixing is a promising method and at the same time it is economical and widely used in rubber industry, so the existing facilities can be utilized without any intervention.

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BS-NS P09

Synthesis and characterization of PANI-TiO_2/epoxy resin nanocomposites

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Epoxy resins are used for a wide variety of protective coatings because of their excellent adhesion, good mechanical properties and their notable chemical resistance under different aggressive environments, such as wet and high humidity conditions [1,2].

The purpose of this study was to prepare polyaniline (PANI) and polyaniline-titanium dioxide (PANI-TiO_2) composites followed by their PANI/epoxy and PANI-TiO_2/epoxy coatings on glass and steel panels to study the physico-mechanical properties and investigate the influence of surface modified polyaniline to commercial epoxy resin.

TiO_2 colloid solution was synthesized by hydrolysis of titanium isopropoxide at 80 ˚C for 8 hours [3]. The PANI-TiO_2 composite was prepared by a chemical oxidation polymerization of aniline using potassium persulphate as an oxidant in presence of colloidal TiO_2 nanoparticles at 0-5 ˚C [4].

The commercial epoxy resin, CHS 210x75, and curing agent, Epicure 3115x70, were mixed in a weight ratio 3:1. Modified PANI/Epoxy films were obtained by adding 1 wt% particles to the epoxy/hardener system. Films of uniform thickness were obtained by applying the composite solutions with wire-wound rods at glass and steel plates and curing them at room temperature for 21 days.

Fourier transformation infrared spectroscopy (FTIR) was used for observed interaction between TiO_2 and polyaniline. Mechanical properties of polymeric films were investigated by the Konig pendulum, cross cut and cupping test. Water vapor transfer through epoxy films were measured by permeability testing cups.

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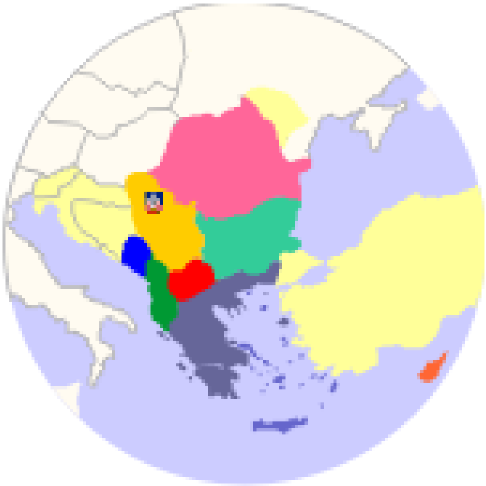
2. ENERGY



O 24 E

Tm(III)-doped δ-Bi_2O_3 for solid oxide fuel cells

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The oxide ion conductors have widely been investigated because of their application in many devices with high economical and ecological interests, such as solid oxide fuel cells (SOFC). δ-Bi_2O_3 polymorph possesses the highest known O^{2-} ion conductivity, which is one to two orders of magnitude higher than that of stabilized zirconia at corresponding temperatures [1]. At the moment, the application of this high-temperature polymorph as an electrolyte in SOFC requires temperatures above 730 °C. However, the doping allows δ-Bi_2O_3 stabilization to room temperature and opens the possibility for construction of SOFC that will operate at intermediate temperatures (ca. 350 °C) [2].

As it is found that some lanthanides are suitable dopants [3], the possibility to stabilize O^{2-} ion conductors related to the δ-Bi_2O_3 polymorph in the Bi_2O_3–Tm_2O_3 system was investigated. Two starting mixtures with compositions $(Bi_{1-x}Tm_x)_2O_3$ (x = 0.04 and 0.20) were homogenized in an agate mortar, heat treated at 750 °C for 3 h and then slowly furnace cooled. The samples were characterized by XRPD, DTA and SEI techniques.

Based on XRPD, the single-phase tetragonal β-Bi_2O_3 was identified in the sample with x = 0.04. Its unit cell parameters, a = 7.742(2) and c = 5.650(2) Å, well-correspond to those of undoped β-Bi_2O_3 [4]. On the other hand, the cubic δ-Bi_2O_3 phase was obtained in the sample with x = 0.20. Its unit cell parameter was greater than the value reported for Tm-doped δ-Bi_2O_3 sample with x = 0.25 [3] (5.5033(9) *vs.* 5.478 Å). Both values are smaller than reported for undoped δ-Bi_2O_3 [4]. This means that the unit cell parameter of cubic δ-Bi_2O_3 decreases as Tm-content increases and it is in accordance with Tm^{3+} and Bi^{3+} ionic radii [5].

For the sample with x = 0.04, cyclic DTA curves showed one reversible β-$Bi_2O_3 \leftrightarrow$ δ-Bi_2O_3 transition with corresponding temperatures: on heating, 660 °C, and, on cooling, 600 °C. Surprisingly, no phase transitions were observed in the sample with x = 0.20 which indicates that the obtained δ-Bi_2O_3 is stable within the whole investigated interval, *i.e.*, from room temperature to 1000 °C.

Electrochemical impedance of δ-Bi_2O_3 phase was measured in the following temperature range: 300 – 800 °C. At higher temperatures (600 – 800 °C) the conductivities are similar (0.11 – 0.32 S cm^{-1}), but with lowering temperature they rapidly decrease, and amount, for example, $2.1\cdot10^{-5}$ S cm^{-1} at 300 °C. As a consequence, two activation energies are found: 0.45(4) eV (600 – 800 °C), and 1.33(2) eV (300 – 600 °C).

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E P01

Comparison of various oil extraction methods from freshwater filamentous green algae

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The algae are an inexhaustible source of the research that offers solutions to many problems of our civilization. The bio-technological applications of algae have become a part of modern reality. One of the many application possibilities is that algae can be used as a renewable energy source. Algae store energy in the form of oil that is suitable raw material for the biodiesel production. Extracting oil from biomass of the algae is one of the most important processes in the production of biodiesel from algae. The main goal of this paper is selection of the most appropriate method and solvent for the extraction of oil from the freshwater filamentous green algae by comparison of the effectiveness of different extraction techniques.

The filamentous green algae collected from freshwater swamps in the vicinity of Nis were used for the research of the lipid extraction metods. The dry biomass of the collected algae was determined gravimetrically. Soxhlet extraction, maceration, ultrasonic maceration (20Khz) and extraction by Bligh-Dyer method were used as the extraction methods, while ethanol, diethyl-ether, n-hexane and a mixture of chloroform and methanol were used as the solvents [1].

The collected biomass had a dry matter content of 15.4 %. Determinated oil content is in range of 3.0 % by maceration with diethyl-ether to 5.4 % which was obtained by maceration with ethanol as a solvent:

Method	Solvent	Algae/solvent	Temp., °C	Oil content, %
Soxhlet	Hexane	1/25	70	4.0
	Ethanol, 96%		80	3.4
Maceration	Hexane	1/20	70	4.1
	Ethanol, 96%		80	5.4
	Dethyl-ether		50	3.0
Maceration, ultrasound	Hexane	1/20	70	4.0
Bligh-Dayer	Chloroform/methanol=1:1	1/5	25	3.7
	Chloroform/methanol=1:2			3.3
	Chloroform/methanol=2:1			3.5

The research has shown that maceration is the most suitable method for oil extraction from freshwater filamentous green algae and the most suitable solvents are ethanol and hexane.

Acknowledgments: This work was funded by Ministry of education, science and technological development of Republic of Serbia, grant No: 45001

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E P02

Kinetic parameters of non-catalytic biodiesel synthesis under elevated pressure: Determination by standard optimisation methods

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Non-catalytic biodiesel synthesis under elevated pressure and temperature is highly efficient in terms of triglycerides conversion, required reaction time and process layout. However, phase equilibrium and mass transfer can play an important role in the final product distribution as well as the presence of reaction intermediates in the final product. This study presents kinetic parameters estimation based on laboratory experiments performed under subcritical conditions in batch reactor, as determined by the standard optimization methods. The kinetic model employed in this study is based on three consecutive and parallel reversible reactions of the second order with six kinetic constants. Although the optimization technique employed for parameter estimation is well known, the development of the specific parameter estimation methodology that employs the results of the available types of experiments is novel and required significant development. The influence of the mass transfer effects was considered as well. The best results were obtained by Genetic Algorithm method for estimation of kinetic parameters. This method resulted in kinetic parameters with improved accuracy in predicting concentrations of important reaction intermediates, i.e. diglycerides and monoglycerides. Activation energies of kinetic parameters obtained by the Genetic Algorithm method are in very agreement with theoretical values determined by molecular orbital calculations.

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E P03

Glycerol derived from biodiesel production as additive in biogas production

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Conventional energetic resources based on the fossil and nuclear fuels are being progressively replaced with renewable energy sources. Production of biogas is a biological process which naturally occurs in the ponds, wetlands and landfills. It offers several advantages concerning resource conservation and environmental protection. Biogas is a product of anaerobic digestion of organic substrates and can be used for treatment of different types of industrial, municipal and agricultural wastes. Another benefit of this process is the production of fertilizer which remains after the digestion process. Biogas is produced by synergistic action of anaerobic acidogenic and methanogenic bacteria. The process is influenced by several factors: organic substrate, temperature, pH value, retention time and mixing. Anaerobic digestion of solid biological wastes is often limited by the long retention time and low efficiency of decomposition of organic solids. For that reason a pretreatment of the feedstock can increase the production of biogas, reduce the amount of volatile compounds and increase the solubility of solid components. This is especially important in the treatment of feedstock with high concentrations of lignin and cellulose. Pre treatment can include mechanical, chemical and biological process. The production rate can be increased by the addition of additives but the additional costs must be taken into consideration. One of the possibilities is the addition of glycerol derived from the production of biodiesel. Glycerol addition can boost biogas yields, but if it does not exceed a limiting concentration in the feed which is defined by the composition of feedstock. Depending of the use of biogas further processing, the removal of carbon dioxide, hydrogen sulphide or water can be necessary. This paper reviews the factors influencing the production of biogas and the use of pretreatment and additives for improving biogas productivity.

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E P04

Phase equilibrium of ethanolysis of triglycerides at high pressure and temperature

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Biodiesel is currently produced by transesterification (alcoholysis – methanolysis or ethanolysis) of various types of edible oils with methanol or ethanol. However, since methanol is mainly produced from fossil sources (crude oil and natural gas) the current biodiesel production leads to only partly renewable transportation fuel production. Furthermore, the depleting fossil sources have raised concerns related to uncertainty of the supply coupled with rising costs of different petrochemical products including methanol. A possible solution to overcome this limitation is to use other alcohols produced from renewable sources, such as ethanol.

Presently, ethanol can be easily produced from biomass that can be found in abundance, via fermentation process, and it is commonly known as bioethanol. Besides that, since there is already commercially production of bioethanol as a substitute fuel for gasoline, the supply of bioethanol for the production of biodiesel could be easily achieved. Somewhat surprisingly, very limited effort has been dedicated to the research on the utilization of ethanol for biodiesel production. This effort is needed in order to provide sufficient body of technical data needed by the commercial biodiesel producers, in order to promote application of bioethanol for its environmental advantages. Since process of transesterification has several technological variants like: homogeneous catalytic synthesis, heterogeneous catalytic synthesis and high pressure non-catalytic synthesis, in case of fatty acid ethyl esters (FAEE) these variants have to be investigated and optimized. The research dedicated to biodiesel production from ethanol via non-catalytic transesterification under supercritical conditions is still very limited and much more information is required for process optimization leading to maximum yields of FAEE biodiesel.

In this study the phase equilibrium of ethanol and triglycerides was determined experimentally. The experimental data were correlated using RK Aspen EOS (ASPEN plus® and UniSim® software packages) in order to identify optimum process conditions. Modelling results obtained using RK-Aspen EOS were found to correlate well the experimental data.

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E P05

Potentials of bioethanol production from some selected local maize hybrids

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Trends of producing bioethanol have been rising and maize is one of the best renewable raw materials for the production of this alternative fuel due to the high content of starch in the grain. Bioethanol is mainly produced from a starchy part of the maize grain leaving significant amounts of valuable by-products such as distillers' dried grains with solubles (DDGS). Due to its high feeding value, high protein and other valuable nutrients, it represents an excellent component for livestock feed mixtures.

Serbia is one of very important maize producers in the world and the surpluses of this cereal grain, which are not used for food and animal feed, should be carefully redirected to the production of bioethanol.

The main goal of the present study was to investigate a suitability of six maize hybrids of a different genetic background developed at the Maize Research Institute, Zemun Polje, Belgrade, Serbia, for bioethanol and DDGS production. For these purposes the physical properties and the chemical composition of grains of the selected maize hybrids, bioethanol yield and the quality parameters of the DDGS remained after the bioethanol production were studied. All six ZP maize hybrids investigated had very different chemical compositions and physical proeprties, which could provide various possibilities of their utilisation. The highest ethanol yield of 94.5 % of theoretical and volumetric productivity of 2.01 g $L^{-1}h^{-1}$ after 48 hours of fermentation were obtained with the hybrid ZP 434 followed by ZP Rumenka, while the lowest ethanol yield and productivity were obtained with ZP 611k. Regarding the chemical composition, all DDGS samples manifested potentially good properties as feed components. The protein content of DDGS samples was high and was more than two-fold higher after fermentaion compared to the kernel protein content. Dry matter digestibility of all DDGS samples was very good in terms of animal feed requirements, as well as the calculated digestible and metabolizable energies.

The hybrid ZP 434 was selected as the most promising ethanol producer. This property may be attributed to the highest level of the soft endosperm fraction, which is more susceptible to starch hydrolyzing enzymes. High yield potential per hectare makes it the best candidate for the commercial bioethanol production because land requirements are minimal. In addition, good quality DDGS is obtained as a by-product. It can as well be potentially beneficial in terms of decreasing of the overall bioethanol production costs by more than 10%.

E P05

Phase equilibria, activity coefficients, excess Gibbs energy and excess enthalpy of two model systems for energetic efficient separation processes design

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For the chemical products industrial manufacturing the highest energy consumption is spent by the separation processes (about 90% from that of the entire technological chain), especially by the fractionating columns. It results that in the design of these processes a special attention has to be paid to the column costs. The thermodynamic data necessary in the design of these equipments, the equilibrium and phase diagram data are of the highest weight in the establishing the number of column plates. Excess enthalpy data are required for the design of the heat exchangers connected to the rectification column. From this point, energetic efficiency of the separation processes depends mainly by the accuracy of the imputed data. They are also necessary for the predictive models development (e.g. modified UNIFAC Dortmund [1] and DISQUAC [2]). In the present work, accurate thermodynamic data (isothermal vapour-liquid equilibria, activity coefficients and excess Gibbs energy at three temperatures, and excess enthalpy at standard temperature) are presented for two model binary mixtures from the family of nitroalkane + chloroalkane, as example necessary data for the separation of pure nitroalkane by chloroalkane from their binary systems. The data modeling was performed by means of Redlich-Kister polynomials, modified UNIFAC and DISQUAC models. Between many other applications, the nitroalkanes are used as stabilizers for chlorinated solvents, which are utilized in dry cleaning, semiconductor processing, and degreasing. The binary mixtures of nitroalkane + chloroalkane systems result from these processes; therefore for their recovery their separation in pure compounds is necessary. The presented data furnish the main information needed for energetic efficient design of the separation process.

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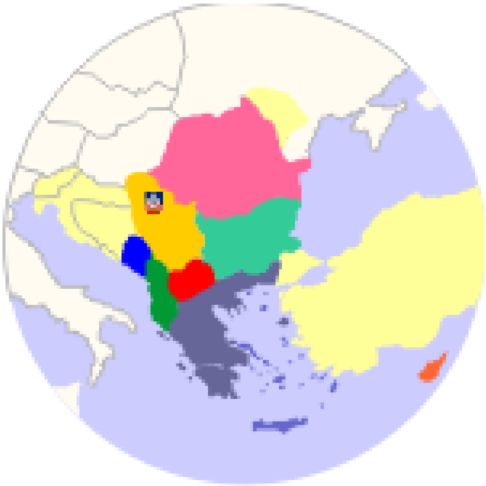
3. RESOURCE EFFICIENCY



O 25 RE

Thermodynamic properties of alkanolamine + alcohol mixtures

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Nowadays, use of aminoalcohols for the hemisorption of greenhouse gases (GHG) presents leading technology in the global efforts for reduction of emission and mitigation of GHG negative effects. Various amino alcohols could be used in the acid gases treatments, in different industries [1]. Densities, viscosities and refractive indices of monoisopropanolamine (MIPA) and 1-butanol and 2-butanol with change of temperature and concentration range was investigated. These properties, especially viscosity and density, are important since, they are incorporated in equations for process and equipment modeling [2]. In addition, excess volumetric and deviation of transport properties give information about molecular interactions present in the investigated system. Numerical thermal expansion model [3], as well as FTIR analysis was used for detailed investigation and description of molecular structure. Linearized Arrhenius equation of viscosities of binary mixtures was used for energies of viscous flows calculation. Data reduction was performed by Redlich-Kister equation. Experimental data with Redlich-Kister equation are presented in Figure 1.

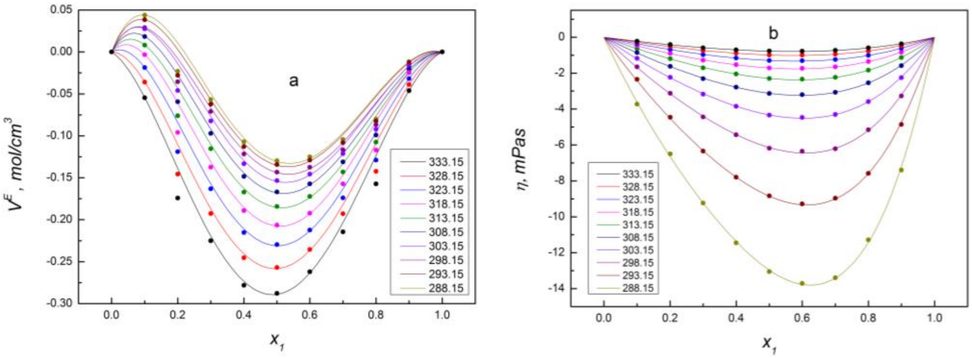

Figure 1. Experimental values (symbols) and Redlich-Kister equation (lines) of a) V^E as function of 2-butanol molar fraction x_1 and b) Δη as function 1-butanol molar fraction x_1.

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RE P01

Densities and viscosities of binary systems with 1-hexanol and tetra ethylene glycol dimethyl ether or N-methyl-2-pyrrolidone, as potential solvents for flue gas desulphurization processes

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Priority task for climate change mitigation is to reduce emissions of greenhouse gases, including sulfur oxides, from stationary power plants. Among wet flue gas desulphurization procedures (FGD), physical or chemical absorption processes followed by solvent thermal regeneration have recently gained more importance [1-3]. For proper equipment design and process optimization, it is necessary to obtain accurate solvent properties data. In this work, densities and viscosities of binary mixtures, 1-hexanol + tetraethylene glycol dimethyl ether (TEGDME) and 1-hexanol + N-methyl-2-pyrrolidone (NMP), as potential sorbents for FGD, have been measured at the atmospheric pressure. The obtained values are presented as a function of temperature and 1-hexanol mole fraction.

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RE P02

Carbon materials from short hemp fibers waste: Surface characterization and heavy metal sorption properties

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The presence of heavy metals in the environment is of a major concern because of their toxicity and threat to humans and other form of life. Heavy metals represent permanent pollutants because they could not be subjected to any degradation process and therefore have tendency towards bioaccumulation. Among many conventional methods that are being used for heavy metal removal, sorption of heavy metal ions onto various solid supports is the most common route applied for decontamination of wastewater and industrial effluents. In the past decade, there is a growing interest in using different type of biomass for production of carbon materials [1] as a sorbents for water purification. In this work, short and entangled hemp fibers, acquired as waste from textile production, were used as low-cost precursor for production of carbon materials. Due to the fact that surface characteristics of carbon material depend of carbon precursor nature, in order to obtain materials with different surface properties, origin short hemp fibers were chemically modified prior to the carbonization. Carbonized hemp fibers surface were characterized by specific surface area and porosity, obtained from adsorption and desorption isotherms of N_2, while the morphology and structure were characterized by scanning electron microscopy. The possibility of using obtained materials in water purification was tested through adsorption of heavy metals. Effectiveness of these carbon materials as a sorbent for heavy metals removal was tested through the sorption of lead ions, and the kinetic data were studied to gain an insight in the process of lead ions adsorption. Additionally, in order to describe sorption process of lead ions and structural parameters of carbonized hemp fibers we have upgraded our previously developed mathematical model [2]. It was found that chemical modification have effect on specific surface area and morphology of carbonized hemp fibers [1] and therefore also affected their sorption properties. Carbonized hemp fibers show good adsorption properties toward heavy metal ions, which is mostly influenced by specific surface area and morphology. A good agreement between model prediction and the experimental data indicates that the proposed mathematical model can be used for optimization of heavy metal ions adsorption process by correlating the model parameters to the carbonized hemp fibers performances.

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RE P03

“Green” method of obtaining polyester-polyols for rigid polyurethane foams with improved physico-mecanical and flame retardant properties

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Sustainability means interacting in ways that do not affect the living systems and the natural resources, i.e: elimination of wastes and toxic emissions, finding renewable sources opposed to classical feedstocks, minimizing energy consumption [1]. In the same spirit, widespread application and non-biodegradability of PET induces a great interest for recycling this material, which is important, as well, for conservation of oil resources, reduction of greenhouse effect and energy preservation [2]. Chemical recycling is the most acceptable technique according to sustainable development principles, because it leads to value-added products. The chemical structure of PET backbone can be modified using suitable co-monomers, conferring targeted properties to the resulting oligoesters [3,4]. The use of 1,4:3,6 -dianhydrosorbitol (isosorbide, IS) monomer in polymers can be motivated by several features, besides it’s provenience from biomass: it is a non-toxic compound, with chiral, rigid molecules [5].

Polyester-polyols were prepared by a “green’ method, consisting in: PET glycolysis with isosorbide, monoesterification of the products with phthalic anhydride, followed by propoxylation, under relatively mild conditions. No by-product or waste resulted, the chemical composition of the products being fully suitable for reaction with diisocyanate, in order to form polyurethane rigid foams. NMR investigations revealed that most of the rigid molecules of isosorbide are linked through at least one ester functional group to an aromatic dicarboxylic acid, thereby forming rigid structural units The polyester-polyols are compatible with polyether-polyols commonly used in rigid polyurethane foams manufacture, forming together long time stable and homogenous mixtures. They can be used up to 30% wt. of the polyol component in rigid polyurethane foams formulations, leading to improvement of physico-mechanical and flame retardant properties of the latter, compared to polyester polyols from PET wastes and usual glycols (diethylene glycol, dipropylene glycol), even obtained using the same synthesis process.

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RE P04

Preparation and characterization of composites based on textile waste

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The aim of this work was investigation of the possibilities of reusing of cotton textile waste, generated during the manufacture in textile industry, as reinforcement in production of composite materials.. The materials used as reinforcement for phenol phormaldehyde resin as matrix have been cotton fabric and cotton textile waste. The composites containing 60 % wt. reinforcement were manufactured by coventional process of compression molding (at pressure of 75 bar and temperature 160 ^{o}C). The mechanical and thermal properties of the produced materials based on textile waste were analyzed and compared to those of commonly used continuous fiber reinforced composites based on cotton fabric and phenolic resin. It was found that the composites based on cotton textile waste are more sensitive to processing cycles with respect to continuous fiber reinforced composites. The mechanical properties of the composites based on cotton textile waste were lower for about 25%, although the thermal stability (determined by Martens method) for both composites reinforced with cotton fabric and with cotton textile waste was similar. The obtained results have shown that cotton textile waste could be reused for production of composites with acceptable mechanical properties, and they could be applied in many industries as construction material with moderate mechanical properties.

RE P05

Bio-based composites produced by conventional techniques using recycled polymer matrix

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In the recent years, the use of renewable resources for the preparation of polymer-based materials has attracted a growing attention because of the increasing demand of environmental friendly materials. Among biodegradable plastics, poly(lactic acid) (PLA) is a very interesting material. It is a degradable thermoplastic polymer with excellent mechanical properties and is produced on a large scale by fermentation of corn starch to lactic acid which is subsequently chemically polymerized. In our previous studies it has been shown that composites based on PLA and kenaf fibers have good mechanical properties, acceptable for the preparation of materials applicable in various areas of construction [1,2,3].

In this paper we have investigated the mechanical and thermal properties of composite materials manufactured from recycled PLA matrix reinforced with kenaf fibers using the conventional techniques, compression and extrusion. For comparison, the composite material manufactured from recycled polypropylene (PP) reinforced with kenaf fibers with identical fiber/ matrix ratio, using the same techniques, was tested. Also, the properties of the composites with recycled matrix were compared to the composites with virgin matrix. Contrary to the recycled PP based composites, recycled PLA based composites have shown significant deterioration in mechanical properties compared to virgin PLA based composites but there isn't significant change in their thermal properties. Further research will be targeted at evaluation of the possibility for recycling of the PLA under the conditions that will not cause major changes in the molecular weight of the polymer.

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RE P06

High pressure density: experimental measurement and modeling

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The experimental measurements of densities of water (Fig. 1), dichloromethane and n-heptane at high pressures were performed using an Anton Paar DMA HP vibrating tube densimeter (Fig. 2) and an Anton Paar DMA 5000 unit as reading device. Vibrating period of the investigated fluids were measured at eighteen temperatures (288.15-453.15 K) and pressures up to 60 MPa. These data were used for calibration of the apparatus [1,2]. In addition experimental density of n-heptane [3] was correlated using Tait equation [4]

$$\rho(T,p)=\frac{\rho_0(T)}{1-C\ln\left(\dfrac{B(T)+p}{B(T)+0.1MPa}\right)}$$

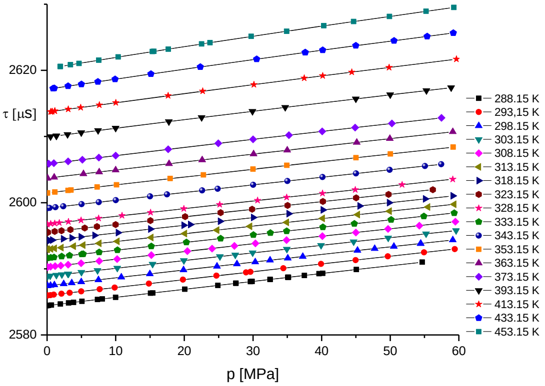

Figure 1. Experimental data of water at T=(283.15-453.15)K and p=(0.1-60) MPa

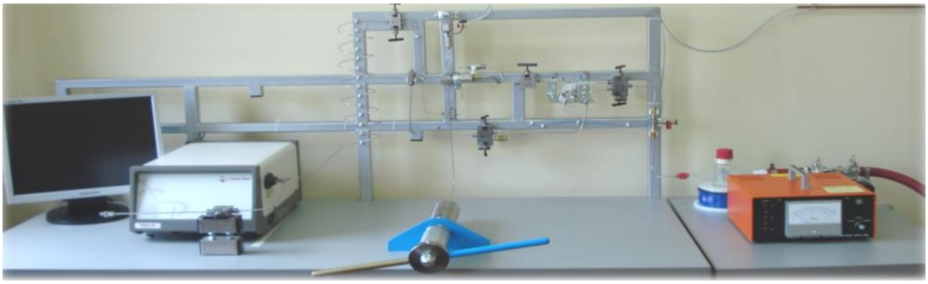

Figure 2. Apparatus for high presssure density measurements

The authors gratefully acknowledge the financial support received from the Research Fund of Ministry of Education and Science (project No 172063).

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RE P07

Applying anaerobic stabilised sludge as a soil conditioner and fertilizer

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The application of anaerobic sludge, post-stabilized or not, as a type of organic fertilizer, has a number of advantages: it directly feeds plants, has a positive influence on soil structure, and increases the soil's agricultural value. The application of anaerobic sludge stabilized with CaO has also been investigated, with results showing that larger yields may be obtained this way, comparable with the yields obtained using chemical fertilizers [1, 2]. During waste treatment, the goal is to improve the quality of sludge as a fertilizer by increasing the nitrogen and phosphours contents and forms [2, 3]. Soil pH is also important, impacting the rates and paths of the chemical and biochemical processes which occur in the soil [1, 2, 4]. In Serbia, brewing and edible-oil refining are the two largest agro-industry sectors and wastes from those industries are not dealt with adequately. In addition, acidic soil spans up to 10% of the developed agricultural land in the country. Therefore, the use of anaerobically stabilized wastes from breweries and edible-oil refineries as a land conditioner and fertilizer was examined. Stabilized sludge (20 g) and sludge post-stabilised by 4% CaO (10 g), were mixed with 300 g slightly acidic soil (pH 6.60; 1500 mg N/kg; 1300 mg P/kg), to improve the pH and nutrient content of the soil. Over 30 days, local autumnal average rainfall was simulated by dosing the sample three times with 300 ml of distilled water. The application of anaerobic brewery sludge as a fertilizer and conditioner was successfull (pH increased by 1.42 and N content by 23%). Sludge post stabilised with 4% CaO also increased the soil pH (by 2.16 pH units), nutrient contents (N by 11%, P by 25%) and nutrient retention, and could therefore be succesfully applied as a soil conditioner and/or fertilizer. The alkalinity of the sludge and the soil pH limited the addition of higher amounts of sludge to the soil. Anaerobic sludge obtained by the digestion of solid edible-oil refinery waste also shows good characterisitics for use as a soil conditioner and fertilizer (pH increased by 1.77, N and P contents both increased by 16%). Edible-oil refinery sludge, post-stabilised with 4% CaO, corrected pH like the post-stabilised brewery slude, but its application is limited by its reduction of the water permeability of the soil, due its quagmire inducing effects. The effect of this sludge on soil quality is small (N content increased by 6%, and total P content by 3%).

Acknowledgment: The authors gratefully acknowledge the support of the Ministry of Education, Science and Technological Development of the Republic of Serbia (project No. III43005and No. TR37004).

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RE P08

Carbon materials from short hemp fibers waste: Surface characterization and heavy metal sorption properties

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The presence of heavy metals in the environment is of a major concern because of their toxicity and threat to humans and other form of life. Heavy metals represent permanent pollutants because they could not be subjected to any degradation process and therefore have tendency towards bioaccumulation. Among many conventional methods that are being used for heavy metal removal, sorption of heavy metal ions onto various solid supports is the most common route applied for decontamination of wastewater and industrial effluents. In the past decade, there is a growing interest in using different type of biomass for production of carbon materials [1] as a sorbents for water purification. In this work, short and entangled hemp fibers, acquired as waste from textile production, were used as low-cost precursor for production of carbon materials. Due to the fact that surface characteristics of carbon material depend of carbon precursor nature, in order to obtain materials with different surface properties, origin short hemp fibers were chemically modified prior to the carbonization. Carbonized hemp fibers surface were characterized by specific surface area and porosity, obtained from adsorption and desorption isotherms of N_2, while the morphology and structure were characterized by scanning electron microscopy. The possibility of using obtained materials in water purification was tested through adsorption of heavy metals. Effectiveness of these carbon materials as a sorbent for heavy metals removal was tested through the sorption of lead ions, and the kinetic data were studied to gain an insight in the process of lead ions adsorption. Additionally, in order to describe sorption process of lead ions and structural parameters of carbonized hemp fibers we have upgraded our previously developed mathematical model [2]. It was found that chemical modification have effect on specific surface area and morphology of carbonized hemp fibers [1] and therefore also affected their sorption properties. Carbonized hemp fibers show good adsorption properties toward heavy metal ions, which is mostly influenced by specific surface area and morphology. A good agreement between model prediction and the experimental data indicates that the proposed mathematical model can be used for optimization of heavy metal ions adsorption process by correlating the model parameters to the carbonized hemp fibers performances.

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RE P09

Oligoester ionomers from PET wastes as dispersing agents for nanocomposites

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The present paper relates to a range of oligoester ionomers derived from PET wastes which can be used in polymer nanocomposites for increasing surface compatibility and enhance phyllosilicate platelets dispersion in thermoplatic resins, especially in polyolefins and butadiene styrene block coplymers, in order to improve their physico-mechanical properties.

It should be pointed out, that PET does not create a direct hazard to the environment but, due to its substantial fraction by volume in the waste stream and its high resistance to the atmospheric and biological agents, it is seen as a noxious material [1]. Therefore, the recycling of PET does not only serve as a partial solution to the solid waste problem but also contribute to the conservation of raw petrochemical products and energy [2, 3].

The synthesis procedure it's a simplified and efficient one, consisting in concomitent glycolysis/transesterification reactions of PET waste with DEG and DMISNa bisglycolesters obtained „in situ", in order to yield terephthalate oligomers with nanofiller-phylic (polar) functional groups: hydroxyl and pendant ionic $SO_3\ ^{-}Na^{+}$ Terminal OH-groups can be subsequently esterified with long chain fatty acids in molar ratios 1:0.6 and 1:1 respectively, in order to accomplish a balanced polar-nonpolar character, thus decreasing the surface tension of the nanoclay and allowing better interactions between organophilic nanofiller and non-polar polymer matrix, as polyolefins are.

The structure, and thermal stability of oligoester ionomers derived from PET wastes were investigated by NMR, FTIR and TGA techniques and interlayer distance of the clay treated with oligoester ionomers, by WAXD. Measurement of surface tension and critical micelle concentration (CMC) revealed that the investigated oligo terephtalate ionomers exhibit a behavior quite similar to classical surfactants, depending mainly on the polar/nonpolar groups ratio within backbone.

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RE P10

Fly Ash/Poly vinyl Chloride composites

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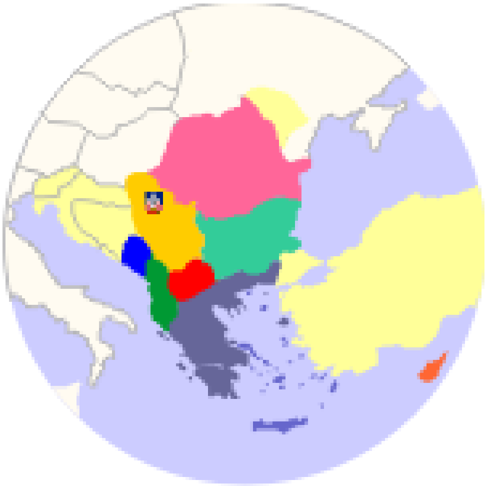
As a by-product from combustion, Fly Ash (FA) waste particles, obtained from the fero-nickel production process as well as from the coal mine, respectively were used as the reinforcement of various matrices. In this work, an atempt was made to produce FA reinforced Poly Vinyl Chloride (PVC) composites aimed for geomembranes.

The effect of flay ash on thermal behavior of PVC based composites was studied. Plasticized PVC was used as a matrix. Concentration of the fly ash was varied in the range of 5, 10 and 20 %. FA/PVC composite samples were prepared using two different types of FA in 1,4-Dioxin with the total mixing time of 30 min. The effect of the FA surface treatment by NaOH and HCl was studied also. The obtained samples were analyzed by TGA/DTA, FTIR, SEM and swelling test.

Uniform reinforcement dispersion in the matrix materials is very important in order to ensure that there was a good interaction between both constituents that will result in good composite's properties. SEM microphotographs of the obtained FA/PVC composites have shown region of well dispersed FA particles, but also and FA agglomerations in the composites. Thermal stability and all the other characteristic thermal parameters of the PVC composites decreased in the presence of both types of FA. Lower values were obtained due to the HCL treatment of FA particles compared to NaOH treated FA. Generally, all the FA/PVC composites have shown higher swelling degree than PVC. Higher values were obtained for composites with NaOH treated FA particles.

4. HEALTH



H P01

Micellar thin-layer chromatography in angiotensin-converting enzyme inhibitors lipophilicity evaluation

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Lipophilicity is one of the most significant biologically active substances properties that attract considerable interest in medicinal chemistry, pharmacokinetics and environmental science. Lipophilicity influences drugs absorption, distribution, binding to plasma proteins and elimination. Thin-layer chromatography (TLC) is known as well established method for lipophilicity evaluation. Angiotensin – converting enzyme (ACE) inhibitors represent the group of drugs widely used in treatment of hypertension. In addition to our previous chromatographic studies of ACE inhibitors [1] in this work lipophilicity of ten ACE inhibitors under conditions of micellar thin-layer chromatography has been examined.

The substances investigated were: **1.** Lisinopril, **2.** Cilazapril, **3.** Enalapril, **4.** Perindopril, **5.** Ramipril, **6.** Moexipril, **7.** Benazepril, **8.** Quinapril, **9.** Zofenopril, **10.** Fosinopril. The experiments were performed on RP-TLC C_{18} plates, commercially available, (Art. 5559, E. Merck, Germany). The plates were spotted with 1μL aliquots of freshly prepared ethanolic solutions (about 2mg/mL) of investigated drugs. The mobile phase was composed of 20% tetrahydrofuran (THF) and 80% phosphate buffer (pH = 6.8) with addition of polyoxyethylene (23) lauryl ether, Brij 35, (0.01-0.06 M). After development, by ascending technique, the detection was performed under UV lump. All investigations were performed at room temperature ($25 \pm 2°$ C).

The increase of micelle concentration in mobile phase led to decrease of retention of all lipophilic investigated substances. Only lisinopril as very polar compound showed increase of retention with increase of micelle concentration. The linear dependences between Brij 35 concentrations and R_M values were established for all investigated compounds. From these linear relationships, values of R_M^0 (intercept) and *m* (slope) were obtained and C_0 values for each solute were calculated ($C_0 = -R_M^0/m$).

The correlations between hydrophobicity parameters R_M^0 or C_0 and KOWWIN log*P* were investigated. The very good correlation with $r^2 = 0.8606$ was established for R_M^0 and KOWWIN log*P* relationship, while for C_0 and KOWWIN log*P* significantly lower correlation was obtained $r^2 = 0.2878$ probably due to micelle’s concentration influence on solutes retention rate.

Acknowledgment: This work was partly supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia as a part of Project TR34031.

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H P02

Steroid dimers-*in vitro* cytotoxic and antimicrobial activities

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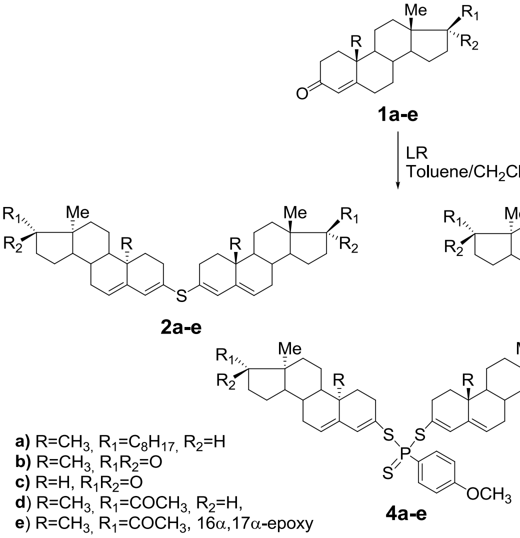
In continuation of our work on modified steroid compounds we have recently reported reactions of α,β-unsaturated steroidal ketones (several cholestane, androstane and pregnane carbonyl derivatives were chosen) with Lawesson's reagent (LR:2,4-bis(*p*-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide) where we described the synthesis of several sulfur and sulfur and phosphorus containing steroidal dimmers [1].



In the present study we have performed extensive *in vitro* antiproliferative activity screening of the previously synthesized steroid dimers **2a-e**, **3a-e** and **4a-e**. These compounds were tested against four human tumor cell lines, cervical carcinoma (HeLa), chronic myelogenous leukemia (K-562) and two human breast carcinoma (MDA-MB-361 and MDA-MB-453 cells). Also, antimicrobial activity against Gram-positive, Gram-negative bacteria and fungal cells, and toxicity to brine shrimp *Artemia salina* were evaluated.

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H P03

Anti-inflammatory properties of *Lactobacillus plantarum* secretory compounds - *in vitro* experiments in gut epithelial functional cell model

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Numerous clinical studies have been made in the past years demonstrating positive effects of probiotics in inflammatory bowel disease as Crohn's disease (1), ulcerative colitis (2) and other gut disorders. Regulation of cytokine production by the enterocytes is believed to be the main mechanism of this probiotic action.

Extracellular metabolites from probiotic *Lactobacillus plantarum* species (PCS22, PCS25 and PCS26) were isolated from cheese and studied for their immunomodulatory properties using *in vitro* functional cell model mimicking gut epithelia (3). Polarized H4 (small intestine) cell line was cocultured on transwell filter inserts with underlying TLT (macrophage) cell line, representing small intestinal model. Inflammation in the cell model was simulated by addition of lipopolysaccharide (LPS) and Interleukin-1β and the inflammation modulatory capacity of bacterial extracellular samples was examined by dot blot measurement of interleukins 6, 8 and 10.

Bacterial metabolites added to H4 cells have lowered IL-6 secretion in TLT cells after provoking inflammation with LPS. Strains PCS25 and PCS26 were the most potent. In addition, bacterial metabolites from PCS26 and LGG strains decreased IL-8 secretion in the IL-1β treated model. However, samples did not cause any difference on the IL-10 secretion.

In conclusion, bacterial metabolites obtained from strains PCS25 and PCS26 posess immunomodulatory effects, as shown in our small intestinal cell model. The exact mechanism of action remains unclear and further research of the mechanisms should be done.

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H P04

Inhibitory effect of 17β-pyrazolin androstene derivatives on steroid hormone biosynthesis *in vitro*

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The 17-*exo*-heterocyclic steroids are able to exert a great variety of biological effects. Several members of this group of compounds inhibit activity of steroid converting enzymes. This antihormonal effect represents potential pharmacological treatment for several androgen dependent diseases – among them; the prostate cancer is the most feared.

We aimed to study the effect of new 17β-pyrazolinylandrostene derivatives exerted on the steroid hormone biosynthesis. For this purpose, we have developed *in vitro* radiosubstrate incubation techniques for the determination of activity and inhibition of $C_{17,20}$-lyase, 17β-hydroxysteroid dehydrogenase type 2 (17β-HSD2) and 17β-hydroxysteroid dehydrogenase type 3 (17β-HSD3) enzymes. Method of $C_{17,20}$-lyase was performed with tritiated 17-hydroxyprogesterone substrate, NAPDH coenzyme and rat testicular homogenate as enzyme source. For 17β-HSD2, ^{14}C-testosterone, NAD and rat liver microsoma were used. 17β-HSD3 activity was measured with the application of ^{14}C-androstenedione, NADPH and rat testicular homogenate. Products of the enzyme reactions (^{3}H-17-hydroxyprogesterone, ^{14}C-testosterone and ^{14}C-androstenedione, respectively) were isolated with thin-layer chromatography and quantified by liquid scintillation counting. Inhibitory effects were calculated from conversions estimated in absence or presence of test compounds.

The investigated twelve compounds (six 5’R and six 5’S epimers) did not inhibit $C_{17,20}$-lyase and 17β-HSD3 activity in the testosterone biosynthetic pathway. Androstenedione producing reverse process catalyzed by the 17β-HSD2 was inhibited most efficiently by the (5’R)-3-chloro-phenyl, (5’R)- and (5’S)-3-cyano-phenyl and (5’S)-3-methoxy-phenyl substituted pyrazoline derivatives. IC_{50} values of these compounds were found 0,93, 1,71, 1,73 and 1,98 μM, respectively.

Our results give a better understanding on the mechanisms of androstanedione and testosterone biosynthesis. Structure-activity relationships observed may contribute to the development of new antiandrogens acting on enzyme level.

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H P05

Ruthenium(II)-arene complex with 6-fluoropicolinic acid: synthesis and characterisation

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Structural diversity of transition metal complexes, their reactions, toxicology and application as drugs are important in the biology and medicine. Disclosure of antiproliferative activity, along with related disadvantages of cisplatine, gave rise to extensive investigations into alternative metal-based anticancer agents. Ruthenium compounds are particularly emphasized because of their cytotoxicity against cancer cells and lower toxicity toward healthy tissues. Pyridylcarboxylate ligands possess asymmetric structure and two different functional groups and act as multidentate ligands and therefore offer great potential as building blocks [1]. Reaction of starting compound [(η^6-p-cymene)$RuCl_2$]$_2$ with 6-fluoropicolinic acid afforded complex [(η^6-p-cymene)Ru(6-F-pico)Cl]. Complex was characterized by elemental analysis, mass spectrometry, IR and NMR spectroscopies. According to these data, ligand coordinates in a bidentate fashion via pyridine nitrogen and deprotonated oxygen of carboxylic group attached to the pyridine ring. X-ray diffraction analysis showed that the molecule adopts a „three-leg piano-stool" geometry (**Fig 1**). Arene ligand forms seat and the chelating ligand along with chlorido ligand are the legs of piano stool. This geometry is common for this type of complexes.

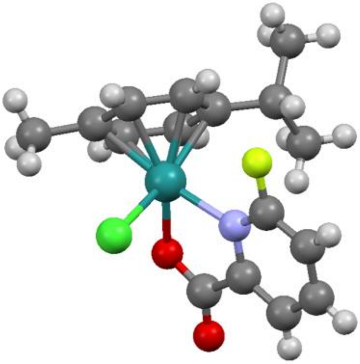

Fig 1. Structure of the complex confirmed by X-ray diffraction analysis

Acknowledgement: This work has been supported by The Ministry of Education, Science and Techological Development of the Republic of Serbia, Grant No. 172017

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H P06

Separation of strontium and yttrium by supported liquid membrane extraction

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Radionuclide ^{90}Y ($T_{1/2}$ = 64.1 h, $E_{\beta,max}$ = 2.3 MeV) is one of the most suitable [illegible]dionuclide for the endoradiotherapy of malignant tumors. ^{90}Sr is an ideal source f[illegible]ng carrier-free ^{90}Y. The separation of ^{90}Y from ^{90}Sr might be achieved by va[illegible] physical-chemical methods, one of them is supported liquid membrane extraction (S[illegible]E). [illegible]ME is based on a three-phase system with an organic phase sandwiched betw[illegible] aqueous phase. In SLME, an organic solvent is held by capillary forces in the pore[illegible] of a hydrophobic porous membrane, between and in contact with two aqueous pha[illegible]nor and acceptor). The processes of extraction and reextraction are achieved in the same membrane module and in the same time. The aim of the present study was [illegible]gate the separation of Y(III) from Sr(II) by SLME in a hollow-fibre contactor under [illegible]ontinuous mode of operation and using di(2-ethylhexyl)phosphoric acid (DEHPA) [illegible]s a [illegible]r in the organic phase.

The separation factor (α) of Y(III) and S[illegible]) [illegible]as determined by clasical liquid-liquid extraction with DEHPA in either n-dodeca[illegible]r hexane. The concentrations of Sr(II) and Y(III) were determining by Inductively [illegible]led Plasma - Optical Emission Spectrometry (ICP-OES). It was found that α depe[illegible]s on p[illegible] of aqueous solution, DEHPA concentration, and the organic solvent. The highes[illegible] (82[illegible]00) was obtained from aqueous solution pH 1 (0.1 M HCl) and 15% DEHPA in n-d[illegible]e.

The SLME was performed in hol[illegible]w [illegible]er contactor [1] containing 7 polypropilene hollow fibers (wall thickness of 5[illegible] an inner diameter of 280 µm, a mean pore size of 0.1 µm, and a porosity of 60%[illegible]effecti[illegible] length of 15 cm. The donor solution (25 mL of 500 ppm Sr(II) and 20 ppm Y[illegible]in 0.1M HCl) was fed along the shell side of contactor in a recirculated mode of oper[illegible]on by a peristaltic pump (4.5 ml/min). The acceptor solution (4 mL of 3 M H[illegible]) [illegible]s fed along the lumen of the hollow fiber in a recirculated mode of operation by a [illegible]ista[illegible]ic pump (0.8 ml/min). The concentrations of both metal ions were determine[illegible]donor and acceptor solutions during the extraction which lasted 6 h.

The remova[illegible]fficiency (R) was defined as the amount of analyte removed from the donor into orga[illegible]ase divided by the initial analyte concentration in the donor phase. The extraction efficiency (E) was calculated as the amount of analyte found in the acceptor phase divided by the initial amount of the analyte in the donor phase. R of Y(III) increases during the SLME and reached the maximum of 85%. E of Y(III) also reised during the SLME, and after 6 h of extraction E is 60%. It means that 25% of extracted Y(III) was captured in the membrane. The changing of Sr(II) concentration in the donor solution was not observed. Also, Sr(II) was not detected in the acceptor phase.

The obtained results show that SLME is an effective methods for separation Y(III) and Sr(II), and for obtaining carrier-free Y(III).

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H P07

Kinetic characterization of Cys34 thiol group of human serum albumin loaded with different long chain free fatty acids

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Human serum albumin (HSA) is the most important transporter of free fatty acids in sera, and about six molecules of the mid and long chain fatty acids (C10 - C18) are bind to one molecule of serum albumin. HSA has one free thiol group located at cystein-34 (Cys34) amino acid residue, and that is very important source of reductive (antioxidant) capacity according to HSA abundance in the plasma. Crystallographic studies showed that accessibility of HSA Cys34 residue to oxidation was significantly changed when free fatty acids were attached to HSA [1]. Therefore, the aim of this study was investigation of the impact of stearic acid (C18:0), oleic acid (C18:1), and fatty omega-3 polyunsaturated fatty acids from fish oil diet supplement EPA (C20:5) [(5Z,8Z,11Z,14Z,17Z)-5,8,11,14,17-icosapentaenoic acid] and DHA (C22:6) [(4Z,7Z,10Z,13Z,16Z,19Z)-docosa-4,7,10,13,16,19-hexaenoic acid] on reactivity of the Cys34 free thiol group. Amount of the free fatty acids bound to HSA was measured with utilized quantitative thin layer chromatography (qTLC) method preceded by Folch chloroform/methanol (2:1) extraction of fatty acids from HSA. Free thiol groups were assayed spectrophotometrically according to the modified Ellman's method (with 5,5'-dithiobis-(2-nitrobenzoic acid as reagent)). Reaction kinetics of free thiol and 2 mM Ellman's reagent were observed during 30 minutes from reaction start [2]. The time course of reaction shows statistically significant difference between reactivity of Cys34 in the presence of stearic acid (with adjusted pseudo-first order reaction constant k' = 0.0175) compared to reactivity of Cys34 of fatty acids freed HSA which was control sample (k' = 0.0048). Also, reactivity in the presence of oleic acid (k' = 0,0196), EPA (k' = 0.0253), and DHA (k' = 0.0158) was greater than control, but surprisingly it was statistically significantly greater than in experiment with stearic acid, thus making possible connection between degree of unsaturration and reactivity of Cys34 thiol group.

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H P08

In vitro evaluation of antiradical activity of pelargonidin, delphinidin and malvin using EPR spectroscopy

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Among cardiovascular diseases hypertension is the most common heart chronic illness which the world has been facing in last number of years. It is characterised by an increase in total peripheral resistance. In addition, reactive oxygen and nitrogen species are directly linked to hypertension. Antioxidant agents can treat oxidative pathologies by neutralising these species, chelating catalytic metals and acting as oxygen scavengers. Because of high incidence and morbidity various drugs have been prescribing for its control. However, these medicaments often possess several side effects. This is the reason why the attention has been focusing more and more toward bioactive natural products and, in particular, to flavonoids including anthocyanidins and anthocyanins.

The aim of this study has been to estimate *in vitro* the antioxidant activity of two anthocyanidins (pelargonidin and delphinidin) and one anthocyanin (malvin – malvidin-3,5-diglucoside) by determining their hydroxyl, superoxide and nitric oxide radicals' scavenging capacities using electron paramagnetic resonance (EPR) spectroscopy. The obtained results and following conclusions will be presented in the conference.

According to the best of our knowledge, this is the first report on anti-nitric oxide radical activity of the anthocyanin malvin which contributes both to the better understanding of its antioxidative properties and the relevant structure-activity relationship studies of the examined class of compounds. Taken all together, the development of new cardioprotective semisynthetic agents with better therapeutic index are reasonable to be assumed.

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H P09

Determination of heavy metal pollution of zeta plain, montenegro

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Recently the problems of environmental pollution by various pollutants, particularly the influence of industry, including heavy metals, has become extremely important. The area of Zeta Plain is the most populated area of Montenegro with a large population and a significant concentration of industrial plants. In Zeta Plain there is an intense road and rail traffic. Next to the main road there is an asphalt base, while civilian and military airports are in the center of the plain. The pollution emitted by the above-mentioned sources differs in type, scope and quantity; therefore the effects are manifested in all parts of the environment. In addition to the above-mentioned, the population of Zeta Plain is engaged in intensive agriculture, and inadequate use of various chemicals is another source of pollution.

The aim of this study was to determine the content of heavy metals, lead, cadmium, copper and zinc in soil samples and plant materials in order to determine the influence of the pollution sources on the environment in Zeta Plain, using plants as bio-indicators of soil contamination. It was also analyzed the content of heavy metals in plant material and their influence on human health through the food chain. At the same time bioavailability of studied metals, the mechanism of their adoption and risk assessment were analyzed by the calculation of bio-concentration factor (BCF) and transportation index (Ti).

The determination of heavy metals content was performed using the technique of atomic absorption spectroscopy. On the basis of the investigation results for twenty soil samples taken from Zeta Plain, it can be concluded that the concentration of toxic metal – lead increased in fourteen soil samples, which is probably a result of the influence of traffic. The investigation results for cadmium and zinc showed that there was no contamination in the investigated soil samples, while the amount of copper increased in one sample. The lack of regulations prevents the qualification of the contamination degree of wild plants with heavy metals. Total load of heavy metals (Pb + Cd + Cu + Zn) in plants is the largest at the location of red mud landfill, which was expected. The investigation results show that the concentrations of the investigated heavy metals in all locations are higher in the soil than in plants. These results indicate that the wild plants in these areas do not belong to the group of metal-accumulators and should not be used for the purpose of phytoremediation.

H P10

Inhibition of tubulin polymerization by (*E*)-4-aryl-4-oxo-2-butenoic acid anilides

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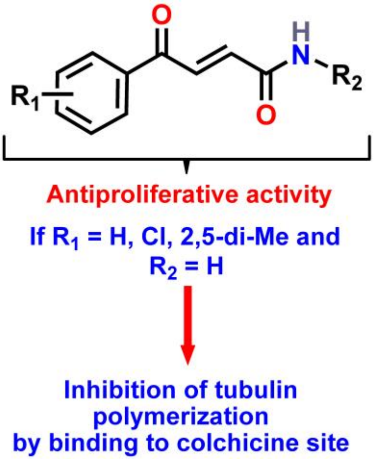
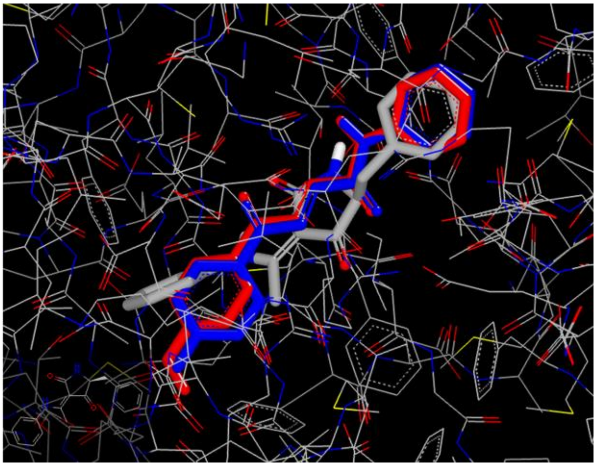
(*E*)-4-Aryl-4-oxo-2-butenoic acid amides (Figure) exerted micromolar to submicromolar antiproliferative activity toward human tumor cell lines *in vitro* [1]. During investigation of molecular mechanism of action, we found that compounds inhibited tubulin polymerization with IC_{50} values below 20 μM. The unsubstituted derivative R_1, R_2=H appear as the most active (IC_{50} = 2.9 μM), while the other effective inhibitors all had small substituents on the aroyl moiety and unsubstituted phenylamide moiety. The highest inhibition of colchicine binding was observed with unsubstitued compound and compounds having 2,5-di-Me and 4-F- substituents on aryl ring. Those compounds were also the best inhibitors of tubulin polymerization. To find possible binding modes, we docked compounds into two crystal structures of tubulin (PDB: 1SA0 and 3HKD) by using two different docking protocols (AutoDock 4.0 and OE Docking). The results obtained showed that anilides are deeply buried into *β*-subunit of tubuline dimer and occupy the same binding site as TN16 ligand (3HKD), lacking any interaction with the *α*-subunit.





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H P11

Simultanous determination of vitamin C and uric acid in human milk from the Serbian breastfeeding women

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Breast milk is the most fundamental source of infant nutrition and provides bioactive agents that protect the babies. Newborns and particularly preterm infants are at high risk of oxidative stress and they are very susceptible to free radical oxidative damage. Therefore, the role of natural antioxidants in breast milk, like vitamin C and uric acid, is of great importance in elimination of reactive oxygen species and providing a good immunity of infants. The aim of this paper was determination of vitamin C and uric acid content in colostrum, transition and mature milk from the Serbian breastfeeding women.

Human milk samples were collected from women in different period of lactation covering colostrum, transition and mature milk. The diluted milk samples were treated with perchloric acid (12%, v/v), vortexed for 1 min and centrifuged at 4000 g for 15 min at 4^{o}C. After proteins precipitation and centrifugation, the obtained samples were filtered and 10 µl was injected into the column. HPLC analysis was performed at Zorbax Eclipse Plus C8 analytical column (3.0x150 mm, 3.5 µm), with the mobile phase consisted of phosphate buffer (20 mM, pH 2.9) and methanol in the volume ratio 95:5 (v/v %). The flow rate was 0.3 ml/min and column temperature was 25°C. Detection was made at wavelength of 244 nm for vitamin C and 280 nm for uric acid. Quantifications of both antioxidants were done by the method of calibration graph.

The concentration of vitamin C in the colostrum obtained from our volunteers were in the range of 0.2 µg/ml-2.0 µg/ml, while in mature milk ascorbic acid concentrations were much higher, reaching in some of the samples values of 15.0 µg/ml. For the uric acid higher amounts were obtained in colostrums and transition milk-average 4.6 µg/ml. The prolonged period of lactation leads to decrease uric acid concentration to1.1 µg/ml.

Vitamin C and uric acid are water-soluble natural antioxidants which concentrations in human milk inversely vary during the period of lactation, providing an optimal antioxidative protection of infants throughout breastfeeding interval.

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H P12

Chitosan-based hydrogels containing silver for antimicrobial application

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Due to its increasing appeal for medical applications, silver is widely used as an antimicrobial agent for various silver-based medical product purposes [1-3]. This paper reports a simple and fast approach to design a new chitosan-based hydrogel containing silver particles. Chitosan was ionically crosslinked with itaconic acid followed by addition of methacrylic acid and crosslinking agent in order to obtain Ch/IA/MAA hydrogel. Chitosan-based hydrogel containing silver (Ch/IA/MAA-Ag) were prepared by immersing xerogel into silver salt solutions of different concentrations. The structure of such system were characterized using Fourier transform infrared spectroscopy. The sorption of Ag+ ions was determined spectrophotometrically, by measuring the silver ions concentration in the salt solution after immobilization experiments. Dynamic mechanical analysis showed good mechanical properties of Ch/IA/MAA hydrogel, while the performed swelling studies confirmed that these hydrogels were pH dependent. The antimicrobial activity of the samples was tested using *E. coli, S. aureus, B. subtilis, E. faecalis* and *Candida albicans* pathogens. It was concluded that the antimicrobial potential was good and was depended on the type of microbes used.

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H P13

Phitochemical profiling by UHPLC-DAD/±HESI-MS/MS analyzes and hepatoprotective activity of *Gentiana cruciata* L. against CCl_4 induced liver injury in Wistar rats

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Many *Gentiana* species are known for their pharmaceutical values, such as *Gentiana cruciata* L., commonly called cross gentian [1]. The dried roots and above-ground parts of *G. cruciata* are consumed in the Balkan region as herbal tea or a medicinal wine for loss of appetite, as a stomachic and component in preparations showing beneficial effects in gall and liver diseases [2]. This study using *in vivo* model investigates hepatoprotective activity of *G. cruciata* aerial part methanol extract (GCA) against carbon tetrachloride-induced liver injury in rats. Wistar rats were orally pretreated with GCA (100, 200, and 400 mg/kg) and silymarin (100 mg/kg) for seven days before they were treated with CCl_4 (1 ml/kg, 1:1 mixture in olive oil) which caused liver injury. Separation, determination and quantification of components in GCA was performed using Dionex Ultimate 3000 UHPLC system equipped with a diode array detector (DAD) and connected to a triple-quadrupole mass spectrometer. Pretreatment with GCA dose-dependently and significantly ($p < 0.001$) decreased levels of serum transaminases, alkaline phosphatase and total bilirubin, whereas an increase was found in the level of total protein compared with CCl_4-treated group. In the liver tissue antioxidant studies, we found a significant increase in the levels of catalase, superoxide dismutase and reduced glutathione, whereas there was marked reduction in the levels of thiobarbituric acid-reactive substances, as compared to CCl_4 treated group. Histological analyses also show that GCA reduced the incidence of liver lesions including necrosis, ballooning degeneration and micro- and macro-vesicular changes induced by CCl_4 in rats. GCA was characterized by the presence of sweroside, swertiamarin, gentiopicrin, loganic acid, isovitexin 4',7-diglucoside, orientin and vitexin, as revealed by UHPLC-DAD-MS and UHPLC-MS/MS analyses. Quantification of targeted compounds in the SRM (selected reaction monitoring) experiment of UHPLC-MS/MS analysis clearly indicated that gentiopicrin (1.067%) was the dominant secoiridoid glycoside in GCA, whereas concentrations of sweroside (0.064%) and swertiamarin (0.033%) were significantly lower.

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H P14

Determination of vitamin E in human milk from the Serbian breastfeeding women in urban region

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Breastfeeding is an important way to ensure ideal food for the healthy growth and development of human infants. Breast milk contains various antioxidants, including fat-soluble vitamin α-tocopherol, that help infants to eliminate reactive oxygen species. It has been demonstrated that the composition of human milk is influenced by race, religion and dietary culture, therefore, it largely varies with geographic, urban and rural regions. The aim of this paper was estimation of vitamin E content in colostrum, transition and mature milk from the Serbian breastfeeding women. Human milk samples were collected from women in different period of lactation covering colostrum, transition-milk and mature milk. All women were from urban region and non-vegetarian.

For the determination, methanol, 0.5% ascorbic acid and 30% KOH were added in this order to 0.5 ml of diluted milk. After vortex-mixing, the tube was left to rest in a water bath at 70^{o}C for 30 min. After the mixture had been cooled, extraction of α-tocopherol was performed using diethyl-ether. The upper layer was carefully pipetted in a new tube and evaporated up to dry in a stream of N_2. The residue was reconstituted in 0.5 ml of absolute ethanol. The obtained sample was filtered and after 30 min 20 µl was injected into the column. HPLC determination was achieved at Restek Ultra IBD C18 analytical column with mobile phase consisted of 100% ACN. The fluorescence detection was made at excitation and emission wavelength of 295 nm and 330 nm respectively. Quantification of *α*-tocopherol was done by the method of calibration graph.

Our results showed that average α-tocopherol content in colostrums was 12.8 µg/ml, while transition and mature milk had amounts of α-tocopherol in the range of 1.1 µg/ml-3.7 µg/ml. These values indicated good quality of milk from urban Serbian women in respect to α-tocopherol. The obtained results showed that stage of lactation is very important factor in vitamin E concentration. It strongly depends on the milk fat content which decreases with the prolonged lactation. The colostrums and colostral milks had significantly higher amount of α-tocopherol than transition and mature milks, providing an important antioxidative protection of newborns in their first days of life.

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H P15

Chitosan/Gelatin based hydrogels for controlled release of lipase form *Candida rugosa*

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Up to day, a significant progress has been made in improving the properties of hydrogels used for drug delivery. However, several challenges remain to improve the clinical applicability of hydrogels for drug delivery, such as the delivery of more sensitive molecules such as proteins, antibodies or nucleic acids.

This paper reports on the characteristics of chitosan/gelatin polymer hydrogels [1] with itaconic acid synthetized with glutaraldehyde as the crosslinking agent, in order to be applied as matrices for enzyme entrapment [2,3]. During the syntheses, the concentration of monomers and crosslinking agent was varied. The matrices were characterized by monitoring the swelling of the prepared hydrogels in various buffer solutions at the temperature of 37 °C. Further, the samples were characterized by FT-IR analysis that confirmed formation of hydrogels, while SEM analysis showed the porous structure of the prepared hydrogels. *Candida rugosa* lipase was used as a model protein in the release experiments that simulated gastrointestinal tract conditions. The results confirmed that the synthetized hydrogels could be used as potential carriers for controlled release of macromolecular drugs, such as therapeutic proteins.

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H P16

Study of **structure-biological** activity relationship of several benzocaine derivatives

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Starting from benzocaine, a well known anesthetic, ten derivatives were synthesized and characterized by UV-Vis, IR, NMR, and elemental analysis [1]. Most of the compounds contain also residues with recognized biological activity, such are nicotinic acid (vitamin B3 or PP), biotin (vitamin B7 or H), lipoic acid (thioctic acid), adamantine [2-5]; the other residues were of crown ether type, benzofurazane, naftylurea, di- and tri-nitrobenzene, and a nitroxide radical. Their biological evaluation included hydrophobicity (lipophobicity), total antioxidant capacity, and some antimicrobial tests. In addition, we found a relationship between the AM1 semiempirical molecular orbital method optimized structures of the new benzocaines and the corresponding biological activities [7].

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H P17

Toxical effects of chloroform in the presents of fulleren C_{60} nanoparticles on *Daphnia magna* midgut

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Carbon nanomaterials have been the subject of extensive research over the past decade because of their use in many commercial products as well as their vast application in agriculture, medicine, electronic industry, cosmetics and others [1]. The molecules of fulleren C_{60} are by their nature hydrophobic and in water they tend to form nano aggregates (nC_{60}). The high adsorptive capacity of nC_{60} can have an impact on transformation and transport of other hydrophobic organic compounds such as naphthalene, phenanthrene, pyrene, pesticides and others [2]. According to US National Toxicology Program's twelfth report, chloroform is classified as carcinogen and is formed together with other disinfection by-products during water chlorination [3]. Suspended nano particles can either increase or decrease bioaccumulation of disinfection by-products [4]. Digestive tract of *Daphnia magna* is well known model system for toxicity evaluation of many diverse nano particles. Considering that nC_{60} can change bioavailability of toxic organic matter, the aim of this study was to examine the effect of nC_{60} in water on toxicity of chloroform on *Daphnia magna* midgut cells. In the experiment there were five groups of daphnids: I - $[nC_{60}]$=40mg/l, II - $[CHCl_3]$=200,8mg/l, III - $[CHCl_3]$=105,1mg/l, IV - $[nC_{60}]$ + $[CHCl_3]$=40mg/l + 200,8mg/l, V - $[nC_{60}]$ + $[CHCl_3]$=40mg/l +105,1mg/l. The size of nC_{60} particles ranged from 320 nm to 2000 nm and the majority of the particles had mean diameter between 316 nm and 631 nm. Particles with diameter < 1 µm represented 76 % of the total number. Addition of chloroform did not affect the size distribution of nC_{60} in the solution after 48 h. Ultrastructural analysis of *Daphnia magna* midgut had shown that nC_{60} aggregates acumulated within gastrointestinal tract as it was expected. Electron microscopy confirmed damages of enterocytes following simultaneous exposure to chlorophorm and nC_{60}.

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H P18

Evaluation of antibacterial activity of some plant species from Romania

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Since ancient times, the antimicrobial properties of plant species from Romania have been commonly used in traditional medicine. In this sense, recent research has emphasized the importance of various substances, which contain compounds with potential effect on pathogens resistant to a number of drugs [1]. Thus, increasingly more plant extracts and their components are investigated for their antibacterial, antifungal and antioxidant proprieties [2, 3].

As consequence, the paper aimed to evaluate the antibacterial activity of some plant extracts derived from arnica flowers (*Arnica montana L.*), pine buds (*Pinus sylvestris*), calamus flowers (*Acorus calamus L.*), redcurrant leaves (*Ribes rubrum L.*) and blackcurrant leaves (*Ribes nigrum* L.).

The extracts were obtained using two methods – water vapor extraction and sonication - both performed in aqueous conditions. The qualitative antibacterial activity of the plant extracts was tested against Bacillus subtilis ATCC 6633 and Escherichia coli ATCC 25922 strains. For this purpose, disc diffusion method was used.

The results showed that all extracts obtained by water vapor extraction revealed antibacterial activity. Thus, the extracts from arnica flowers showed the highest antibacterial activity, the diameter of inhibition being 10 mm. The experiments done on extracts obtained by sonication did not show positive results.

Preliminary data support the water vapor extraction method for the valorification of plant active compounds in terms of using them as natural therapeutic agents.

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H P19

Antimicrobial activity of eco-friendly dyed cotton by *chamomillae flos* extract

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The growth of microorganisms on textiles inflicts a range of unwanted effects not only on the textile itself but also on the wearer. Those effects include the generation of unpleasant odour, stains and discoloration in the fabric, a reduction in fabric mechanical strength and an increased likelihood of contamination.

Antimicrobial finishes of textile materials have become necessary for enhancing apparel performance along with meeting consumer - led future demands. Many commercial products are currently available in the market with the range of antimicrobial properties for textile industry. Majority of such products are synthetic based and may not be environment friendly.

Natural dyes which presents in plants are less harmful on humans and environment so they play an important role to be a better alternative source to synthetic dyes.

Numerous reports suggest that *Chamomillae flos* has wide spectrum of biological and pharmacological activities including antioxidant, antibacterial, antifungal, antiviral, antitumor, anti-inflammatory, anti-coagulant activities.

Enzymatic scoured cotton knits with alkaline and acid pectinase were dyed with *Chamomillae flos* extract in combination with several mordant.

The antimicrobial efficiencies of all fabrics were assessed according to AATCC test method 100 - 2004. The gram-negative bacteria *Escherichia coli* (ATCC 25 927) and fungal strain *Candida albicans* (ATCC 10 231) were used as test microorganism, because they are the most often cause of the intra-hospital infections over the world.

H P20

Potentiometric determination of pK_a values of ACE inhibitors

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ACE (angiotensin-converting enzyme) inhibitors are drugs applied in the treatment of different cardiovascular disorders, primarily in the therapy of hypertension and congestive cardial insufficiency. The presence of peptide bond and free carboxyl group is a common structural feature of the ACE inhibitors. The latter group in ionized form is responsible for the interaction with a protonated amino group of the arginine residue in the cationic active enzyme site. In addition to carboxyl group, ACE inhibitors can contain some other ionizable groups such as primary and secondary amino groups and sulfhydryl group, giving them the properties of acids or ampholytes.

pK_a value represents an important parameter in physico-chemical characterization of pharmacologically active substances and it is of the utmost importance for the estimation of their behavior in vitro and in vivo. Knowledge of drug pK_a values is significant not only for analytical procedures, but also in pharmaceutical industry in development of novel pharmaceutical dosage forms. Drug absorption, distribution, metabolism and elimination (ADME) depend on the degree of their ionization. pK_a Values of ACE inhibitors published so far were mostly calculated applying computer programs and only in a few cases these values were experimentally determined (captopril, enalapril, lisinopril). This prompted us to determine pK_a values of nine most frequently prescribed ACE inhibitors such as captopril, cilazapril, enalapril, fosinopril, lisinopril, perindopril, quinapril, ramipril and zofenopril.

Determinations of pK_a values were performed at 25 ^{o}C and constant ionic strength of 0.1 M (NaCl). Due to a slight fosinopril solubility its pK_a value was determined in 50 % (w/w) methanol-water mixture. A computer program Hyperquad was used to derive pK_a values from the data obtained by potentiometric titrations. The pK_a values of carboxyl group (pK_{a1} and pK_{a2} of lisinopril and pK_{a1} for the other examined ACE inhibitors) ranged from 1.43 – 4.72. Since lisinopril molecule contains two carboxyl groups (terminal and proximal), pK_{a1} of 1.43 can be ascribed to more acidic proximal carboxyl group. The obtained pK_a values of the secondary amino group (pK_{a2} of cilazapril, enalapril, quinapril, perindopril and ramipril, and pK_{a3} of lisinopril) ranged from 5.40 – 7.20. It has been observed that among the examined ACE inhibitors, only lisinopril and captopril participate in protolytic equilibria even at high pH of the media. The pK_{a4} of the primary amino group of lisinopril was 10.90 and pK_{a2} of the thiol function of captopril made 9.99.

Keeping in mind that drug bioavailability is directly correlated with distribution of equilibium forms, percentage of equilibrium forms of the examined ACE inhibitors can be calculated on the basis of pK_a values.

H P21

Antioxidant activity of some flavones evidenced by chemiluminescence method

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The work aims to simulate *in vitro* the effects caused by oxidation of five hydroxiflavones (HF) (some typical models of flavonols), (3 - HF, 6 - HF, 7-HF, 3, 6 - diHF and 3, 7 - diHF) using the chemiluminescent system luminol-hydrogen peroxide, in phosphate buffer, pH 7.4. The contribution of bovine and human serum albumins to the antioxidant activity of the mentioned flavones, in the chemiluminescent system luminol-hydrogen peroxide, has been also investigated. The results are discussed with relevance to the oxidative stress process.

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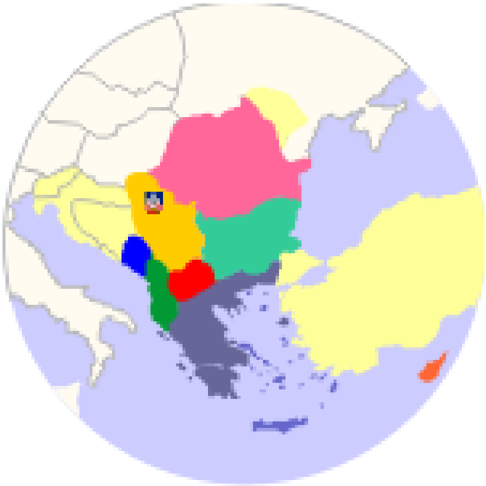
5. FOOD



O 26 F

Mineral content of Serbian propolis as a tool in tracing regional differences

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Propolis is a resinous material of complex composition. It is collected by honeybees from sprouts and plant exudates and modified in the beehive by the addition of salivary secretions and waxes. Propolis sample can contain more than 300 components, depending on the plant source and its geographical origin. The major compounds present in propolis are resins, mainly composed of flavonoids, phenolic acids, and esters, which often form up to 50% of all the ingredients. The composition of propolis is completed by waxes (30%), volatile essential oils (10%), pollen (5%), and other organic and inorganic compounds (5%). Propolis is one of few natural products which are offered today with valuable nutritional and medicinal qualities. These properties are determined, among others, by its mineral components. The mineral content of propolis is influenced by the content of the minerals in the soil, climatic factors (temperature, humidity, wind), and also by the degree of pollution in areas visited by the bees.

The mineral content of the Serbian propolis have not insofar been analyzed despite the long tradition of its production. The aim of the present study was to characterize propolis samples from different locations of the Serbia as well as to evaluate similarities and differences among them by the application of chemometric tools. Therefore, 54 samples of propolis were collected from seven regions of Serbia. Determination of the 22 heavy metals and trace elements was performed using optical emission spectrometry with inductively coupled plasma (ICP-OES) technique. It can be noted that potassium is the most abundant component considering all of studied samples, calcium is the second one, followed by magnesium, iron, zinc, aluminum, and sodium. The minor and trace elements include titanium, manganese, boron, copper, nickel, plumb, and strontium.

Kruskal-Wallis test was applied to differentiate groups of samples according to geographical origin of propolis. Based on the results a significantly higher content of zinc was observed in East region and Vojvodina. Also, Central region was differentiated from East, West and South regions by the content of potassium, and magnesium.

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O 27 F

Inhibition of actinidin, a kiwifruit cysteine protease, influences immunogenicity, conformation and digestion stability of this allergen

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Kiwifruit has recently emerged as one of the top ten food allergy sources, making it a good example of the possible consequences encountered by introducing a novel item into the human diet. The mechanism of sensitization through the oral route is not yet understood, although it has been postulated that food allergens must be able to resist denaturation and proteolytic degradation during their passage through the gastrointestinal tract. The major allergen of kiwifruit is actinidin, a cysteine protease of the papain family present in abundant quantities in the pulp of this fruit.

In this study we first evaluated the IgE-binding properties of biologically active and thermally inactivated actinidin. Although it was capable of inducing clinical symptoms *in vivo* in skin prick tests, we failed to detect IgE reactivity of active actinidin in Western blot with patient sera. Thermally inactivated actinidin exhibited IgE reactivity both *in vivo* and *in vitro*; indicating that heat processed kiwifruit products may induce clinical reactivity. We further showed that actinidin preserves an intact primary structure after 2h of simulated gastric digestion, followed by 2h of simulated intestinal digestion, as assessed by SDS-PAGE and ESI-TOF analysis. Zymography analysis and immunological assays confirmed that actinidin also preserves proteolytic activity and immunogenicity after exposure to digestive conditions. In comparison to active actinidin, inhibition of this cysteine protease with a specific irreversible inhibitor (E-64) led to dramatic changes in the digestion stability and inactivated actinidin was fully degraded after only 1h of pepsin treatment. Results from CD spectroscopy and ANS binding spectrofluorimetry assays showed a difference in the conformation of active and E-64 inhibited enzyme. Molecular dynamics simulations indicated that binding of E64 triggers conformational changes of the protein at the part relatively close to active site Cys-25. The described features of active actinidin and the structural changes upon inhibition of this cysteine protease could be significant in elucidating the oral route of sensitization for this allergenic protease.

O 28 F

Biochemical and functional properties of egg white hydrolysates produced by different proteases

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Enzymatic hydrolysis of egg white proteins (EWPs) has shown a great potential to improve their functional properties such as increased solubility, stability, and digestibility while still retaining their nutrition value. The high selectivity and mild reaction conditions associated with the enzymatic process have made this approach an attractive alternative in the production of EWPs with improved functional properties, which are often difficult to obtain by conventional chemical route. Moreover, the inherent specificity of various proteolytic enzymes should control the nature and extent of hydrolysis and thus the functional properties of the product.

The focus of this work is to find the best combination of enzymes and the mode of both substrate pretreatment and process implementation for improvement of the overall hydrolysates` quality. For this purpose EWP solution was hydrolysed with several enzymes using both, one-step and two-step hydrolysis in a stirred stirred-tank reactor employing an enzyme to protein substrate weight ratio previously selected to obtain the desired level of conversion in the first step within a time period from about 20 to about 75 minutes depending of protease used. The obtained hydrolysates were then tested on antioxidant activity, flavour, solubility, digestibility emulsifying activity, foaming capacity and stability. Selected results have been presented in Figure 1.

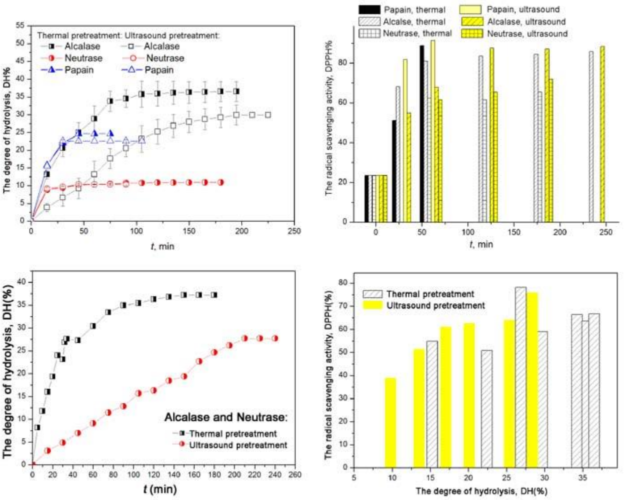

Figure 1. The effect of substrate pretreatment and protease type on EWPs hydrolysis

The application of two-step enzymatic process, based on the use of the bacterial alkaline protease in the first step, and then the introduction a more specific protease in the second step to selectively reduce the bitter peptides, seemed to be advantageous.

O 30 F

Molecular characterization of recombinant Mus a 5 allergen from banana fruit

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Allergy to banana fruit appears to have become an important cause of fruit allergy in Europe. Among five allergens that have been found, Mus a 5 was identified as a candidate allergen for the component-resolved allergy diagnosis of banana allergy. Because of the variations in protein levels in banana fruit, in this study Mus a 5 was produced as a fusion protein with glutathione-*S*-transferase (GST) in *Escherichia coli*. Thirteen patients with clinical history of allergic reactions to banana were included in the study. IgE-mediated allergy was documented by case histories, SPT and / or positive specific IgE (CAP-FEIA,) to banana.

The coding region of Mus a 5 cDNA (939 bp) was cloned into the expression vector pGEX-4T and transformed into *E. coli* BL21. Recombinant Mus a 5 cDNA encodes a protein of 541 amino acid residues with predicted molecular mass of 60143 Da and calculated p*I* of 5.65. The recombinant protein was extracted from the bacterial cell lysate and thereafter fractionated on GST affinity column. After elution from the affinity matrix, rMus a 5 was purified by ion-exchange and reversed phase chromatography. The yield of purified rMus a 5 was about 10 mg per liter of the cell culture.

The identity of the construct was confirmed as the first five amino acids determined by Edman degradation (MSPIL). By mass fingerprint peptides with sequences matching that of rMus a 5 were identified by MASCOT program covering about 55 % of the protein primary structure. IgG reactivity of recombinant protein was shown in 2-D immunoblot with anti-Mus a 5 antibodies, while IgG binding to natural Mus a 5 was inhibited with the recombinant Mus a 5 in immunoblot inhibition. IgE reactivity of recombinant Mus a 5 was shown in a group of thirteen persons sensitized to banana fruit.

Recombinant Mus a 5 is a novel reagent suitable for the component-resolved allergy diagnosis of banana allergy.

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F P01

Protective effect of *Filipendula hexapetala* Gilib. root extract on lipid oxidation in different model systems

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Filipendula hexapetala Gilib. is a perennial, rhizomatous herb, 30–80 cm high, growing in dry grasslands, widespread in Serbia [1]. Extracts of *Filipendula* species (Rosaceae) have been used in traditional medicines of Europe and other countries as anti-inflammatory, analgesic, antirheumatic, diuretic, astringent, and diaphoretic agents. Due to the high content of tannins in the roots *F. hexapetala* is frequently used to treat stomachache and diarrhea [2]. The aim of this study was to examine antioxidant activity of methanolic root extract of *F. hexapetala* on lipid oxidation in different model systems as a potential source of natural antioxidants. Antioxidant activity was determined as the degree of inhibition of lipid peroxidation in linoleic acid emulsion [3], in β-carotene/linoleic acid-bleaching system [4] and a TBARS assay was used to measure the potential antioxidant capacity of the extract, using egg yolk as a a lipid-rich medium [5]. Also, the content of condensed tannins was determined with precipitation of proanthocyanidins with formaldehyde [6] and the content of gallotannins was determined with the potassium iodate assay [6]. Tested extract showed a high level of inhibition of lipid oxidation in linoleic acid emulsion (IC_{50}=18.77 µg/mL), in β-carotene/linoleic acid-bleaching system (IC_{50}=998.82 µg/mL) and in egg yolk-model system (IC_{50}=1227.98 µg/mL), compared to natural antioxidants such as gallic acid, ellagic acid, quercetin, rutin and standard antioxidant BHT. The amounts of condensed tannins and gallotannins recovered were 1.15 and 48.53 mg GA/g dry extract, respectively. The lipid peroxidation causes falling-off in quality of lipid containing foods, and induces oxidative damage to the cell membrane in a biological system. These results showed that investigated root extract of *F. hexapetala* can be a source of natural antioxidants and may find application in biological systems and food products.

This research was supported by the Ministry of Education and Science of the Republic of Serbia (project No. III 43004).

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F P02

Kinetic model of the hydrolysis of egg white proteins by Alcalase

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The kinetics of hydrolysis of egg white proteins by Alcalase 2.4L (protease from *Bacillus licheniformis*) was investigated. In this paper, the main objective was to determine the appropriate empirical model for the proteolytic hydrolysis of egg white. A logarithmic equation $X = (1/b) \ln (1 + abt)$ indicating the relationship between the degree of hydrolysis (DH) and time was established. Experimental data were successfully fitted with kinetic model taking into account the enzyme inactivation and substrate inhibition, and related kinetic constants were determined. The kinetic study was performed at optimum process parameters: initial enzyme concentration of Alcalase 2.4L, initial substrate concentration of the egg white proteins and different temperatures of the reaction. The kinetic and thermodynamic constants for reaction of hydrolysis (K_i = 320.07 mg cm^{-3}, k_2 =0.0104 min^{-1}, k_d = 0.0743 min^{-1}, E_a = 103.04 kJ mol^{-1}, E_d = 99.52 kJ mol^{-1}) were responsible for the empirical equation. Kinetic constants of the hydrolysis were determined, and good congruence between the model and experimental data was achieved. The results of nonlinear regression of the proposed kinetic model agreed with the experimental data, thus the kinetic equations can be used to fit the enzymatic hydrolysis process of egg white protein and to optimize the operating parameters for the bioreactor design.

F P03

Assessment of genotypic variation in water-soluble carbohydrate accumulation in wheat

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During vegetative and early reproductive growth of small grain cereals, including wheat, assimilated carbon is accumulated temporarily in the stem and leaf sheath as carbohydrate reserve [1,2]. These reserves could improve yield stability by providing an alternative source when photosynthetic capacity is limited such as during the later phases of grain filling or during periods of abiotic stress [3,4]. Fructan and sucrose are the main reserve carbohydrates in vegetative parts of wheat and are often designated as water-soluble carbohydrates to distinguish them from the structural carbohydrates present in cell walls [1].

With the aim to investigate spatial capacity of water-soluble carbohydrate storage in enclosed and exposed part of the peduncle we assessed 45 wheat genotypes grown during two consecutive seasons in field experiments. In the early generative phase (9-10 days after anthesis) stems of 3 plants per genotype were sampled [1]. The extraction [5] and analysis of water-soluble carbohydrate was performed and the results were expressed as fructose equivalents on dry matter basis [6].

Wheat genotypes of higher water-soluble carbohydrate accumulating capacity were identified. This finding could be important for further investigation in selection of genotypes exhibiting greater ability for accumulation of carbohydrates in stem with the aim to increase yield in stress conditions.

The study was financed by the Serbian Ministry of Education, Science and Technological Development (TR31005).

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F P04

Principal component analysis (pca) of trace elements in the mussel *M. galloprovincialis* collected in the coastal area of southeastern Adriatic

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PCA was performed to identify a common source for heavy metals. In this study mussel samples have collected from the costal area of southeastern Adriatic Sea in two years at the same locations and analyzed in order to determine the concentration and origin of the next trace elements: Cr, Fe, Mn, Zn, Cu, Ni, Co, As, Pb, Cd, and Hg. The complexity of eleven elements data in the investigated twenty-four mussel samples was reduced by PCA. The results indicate that the four PC components explained about 76.3 % of the total elements variability in examined mussel samples: Fe, Mn, and Zn, are in positive correlation with the PC1 component (27.5%); Cu, Ni, and Co are positively and As negatively correlated with PC2 (20.6%). The PC3 is defined completely as anthropogenic impact with positively Hg, Cd, and Pb loadings (15.7%) and the fourth factor is correlated with Cr and explains 12.5% of the total variability. The PCA results showed that among all mussel samples, taken from five different locations in four different seasons, there were major discrepancies temporally, but not locally, related to determined trace elements.

F P05

Polyphenols and anthocyanins determination in juice, pulp and whole fruits of strawberry, raspberry and blackberry of the West-Serbian origin

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Strawberry (*fragaria versa, fragaria ananassa*), raspberry (*rubus idaeus*) and blackberry (*eubatus focke*) are season berries, with attractive odor, color and aroma. These sensory and organoleptic properties come from micronutrients and phytochemicals, which constitute nutritive and bioactive values of berries together with dietary fibers. Polyphenolic content is important because of the strong antioxidative effect on free radicals, which are either scavenged or complexed with metal precursors forming helate compounds. Free radicals are normal products of human metabolism which initiate a number of cardiovascular, degenerative and proliferative diseases.

The total polyphenols and anthocyanins in berries (strawberry, raspberry and blackberry) of the West-Serbian origin are determined. The berries were firstly frozen for storage, then spontaneously defrosted before each analysis. Previously, different alkyl-alcohols (C_1-C_4) and acetone were investigated in order to find the best extracting solvent for polyphenols. The berry polyphenolic extracts were obtained from the fruits (juice, pulp, whole fruits) by extraction with pure methanol. 1 g of the fruit material was mixed with 5 ml methanol and mechanically stirred for 15 minutes at RT. During this extraction a flocculent aggregation of pectin occurred, hence the polyphenolic extracts were separated by centrifugation. An aliquot of berries was taken away to separate the juice and pulp by pressing and centrifugation. Different alkyl-alcohols and acetone were investigated in order to find the best extracting solvent for polyphenols. The berry polyphenolic extracts were obtained from the fruits (juice, pulp, whole fruits) by extraction with pure methanol. 1 g of the biologic material was mixed with 5 ml methanol and mechanically stirred for 15 minutes at RT. During this extraction a flocculent aggregation of pectin occurred, hence the polyphenolic extracts were separated by centrifugation. The content of polyphenols and anthocyanins in the methanolic extracts of berries and their respective parts (pulp and juice) was determined with spectrophotometric methods. The antioxidative activity of the whole berries was determined with the DPPH-method. It was found, that blackberry showed the strongest antioxidant activity (EC50=4.05 mg), having the most total polyphenols (2044 mg/kg) and anthocyanins (1095 mg/kg). Regarding particular parts of berries, it was found, that pulp generally possessed more polyphenols than juice (excepting strawberry, where the distribution was equal).

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F P06

Elemental composition of maize grain from organic production

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Organic agriculture means production of high quality food or raw by using of natural potentials of plants (stress tolerance, pest tolerance, optimal usage of present environment) with maintaining of soil quality. It is based on controlled input of defined agrochemicals, mainly natural products, like plant extracts, fertilizers originated from decomposed organic products or manure also from organic cattle production. The aim of experiment was to examine impact of different production systems on grain quality of red grain maize variety (Rumenka), which include organic cropping with application of organic fertilizers: DCM EKO-MIX 1 (N:P:K=9:3:3, 65% organic matter - NPK1) and DIX 10 N (N:P:K=10:3:3, 72.5% organic matter - NPK2) in amount of 500 kg ha^{-1}, control (without fertilization) and conventional cropping (incorporation of 163 kg urea ha^{-1}, with standard usage of the pesticides) during 2012. Experiment was set up in rain-fed conditions on chernozem soil type. Weeds were removed in organic field manually by hoeing. Beside the yield parameters, nutritive quality of maize grain was presented with its elemental composition which was analysed by Inductively Coupled Plasma - Optical Emission Spectrometry.

Growing season of 2012 was highly stressful for plants with maximal average temperatures over 30°C and sum of precipitation of only 57.3 mm during June-August (anthesis and grain filling period). Irrespective to absence in using of the pesticides in organic productions, achieved yield and 1000 grains weight were higher averagely to 30% and 12%, respectively, compared to conventional production. Moreover, all three organic treatments had positive impact on K, Mg and Mn assimilation, with their higher values in grain, compared to conventional cropping (in average 26%, 22% and 20%, respectively). When contents of N and P as macronutrients and Cu as micronutrient were considered, NPK1 treatment increased their content up to 7%, 6% and 18%, respectively, while in the other two organic treatments, N, P and Cu contents were negligible lower, compared to conventional cropping. It was interesting that Ca, Fe and Zn contents were lower in grain of maize from organic cropping (on average 72%, 17% and 46%, respectively). On the other hand, when nutrients uptake with yield was considered, it could be assumed that higher amounts of all analysed elements were outtake from field in organic production.

Based on preliminary data of this study, it could be concluded that in rain-fed cropping differences in yielding between organic and conventional production were negligible, but the differences in chemical composition of the produced grain were high, giving advantage to organically produced maize grain, as a source of N, P, K, Mg, Cu and Mn.

F P07

HPLC method for the quantification of flavanols and procyanidins in milk chocolate samples and correlation to total antioxidant capacity

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Cocoa powder and chocolate are made from the dried seeds that are found in pods on the cocoa tree (*Theobroma cacao*). Cocoa beans are a concentrated source of antioxidants [1] and flavonoids, with the flavan-3-ols being present in high concentrations [2], and procyanidins as the oligomeric and polymeric catechin [3].

The aim of this research was to evaluate the total polyphenol and flavonoid content as well as antioxidant activity of nine milk chocolate. Milk chocolate is the predominant form of chocolate consumed in Serbia and contains 27-30 % of cocoa mass. The Folin-Ciocalteu reagent was used to determine total polyphenols (λ=760 nm). Gallic acid (GA) was used as a calibration standard and the data were expressed as milligram gallic acid equivalent per gram of choholate (mg GAE/g) and ranged from 2.84 to 5.59 mg GAE/g. The total flavonoid content was determined according to the aluminium chloride spectrophotometric method (λ=510 nm), using catechin as a standard, and ranged from 1.73 to 3.70 mg CE/g. The antioxidant capacity (AC) of chocolate samples were analyzed using four different assays based on different chemistry: DPPH radical scavenging activity (ranged from 6.46 to 13.01 µmol TE/g), ABTS radical cation scavenging activity (ranged from 0.063 to 0.145 µmol TE/g), FRAP ferric reducing-antioxidant power (ranged from 13.38 to 30.35 µmol FE/g) and RP reducing power assay Fe(III) to Fe(II) (ranged from 56.69 to 146.69 µmol of ACE/g).

Individual phenolic compounds analysis using HPLC-fluorescence detection method. Using HPLC method the following groups of phenolic compounds are identified and quantified: phenolic acid (protocatechuic acid), flavan-3-ols ((+)-catechin and (-)-epicatechin) and procyanidins (procyanidin B_1, procyanidin B_2, procyanidin B_3 and procyanidin B_4). Identification was carried out by comparating the retention times and spectral data with those of standards.

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F P08

Osmotic dehydratation of pork meat – The artificial neural network model

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Mass transfer of pork meat cubes *(M. triceps brachii), shaped as 1x1x1 cm*, during osmotic dehydration (OD) and under atmospheric pressure was investigated in this paper. The effects of different parameters, such as concentration of sugar beet molasses (60–80%, w/w), temperature (20–50°C), and immersion time (1-5 hours) in terms of water loss (*WL*), solid gain (*SG*), final dry matter content *(DM)* and water activity (a_w) were investigated, using experimental results. Mass transfer is caused by a difference in osmotic pressure: water outflow from product to solution, solute transfer from solution into the product, and leaching out of the products own solutes. Sugar beet molasses is known as an excellent medium for OD, primarily due to the high dry matter (80%) and specific nutrient content.

An artificial neural network (ANN) model was developed for the prediction of *WL*, *SG*, *DM* and a_w in OD of pork meat cubes. Analysis for variance (ANOVA) were conducted for linear model of process variables, and response variables were tested against the impact of these variables. A significant effect $p<0.05$ of all variables, and r^2 for *DM* and *WL* were found to be very acceptable. All four variables considered in the ANOVA analysis, were used for the ANN modeling. These models were able to predict process outputs with r^2 of 0.952 for *SG* and r^2 0.980 for *WL*. According to standard score analysis, it was noticed that the optimal number of neurons in the hidden layer is seven, when obtaining high values of r^2 and also low values of sum of squares criteria. The wide range of processing variables considered for the formulation of these models, and their easy implementation in a spreadsheet calculus make it very useful and practical for process design and control. As compared to multiple regression models, ANN models yield a better fit of experimental data, and they can be effectively used for predictive modeling and optimization of OD processes.

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F P09

The effectiveness of oxidizing agents **in** the removing of organic matrix of sugar beet molasses

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Commercial sugar beet molasses (SBM) have an average water content of 20%, and organic materials in a range from 72 to 77%, with a total sugar as saccharose in a level of about 51% [1,2]. Preparation of appropriate solution, suitable for elemental analysis, in case of molasses is challenging task. Sample preparation was performed by thermal treatment at 350°C and associated wet acidic treatment at 160°C which make a cycle of combined treatment (T-A-treatment). The cycles of T-A-treatments were repeated to obtain the white sediments that were dissolved in 0.07 M HNO_3. In acidic treatment combinations of HNO_3 and different oxidising agents (OA) like H_2O_2 and HCl were applied. The aim of this work was to investigate the effectiveness of various combinations of oxidizing agents in the T-A-treatment. During this experiment we treated 3.0±0.1 g molasses for each test. Combination of oxidizing agents was defined by exactly determined portion. For a given combination of OA_i, corresponding portion includes: p_i=3 mL HNO_3 + 1 mL K_i, where $K_1 = HNO_3$, $K_2 = H_2O_2$ and $K_3 = HCl$. In this way, portions differ only in the type of K_i. Corresponding consumption of oxidizing agents in each cycle of T-A-treatments is defined as a dose of OA (D_{OA}). Accordingly, the dose of OA used in one cycle is $D_{OA} = D_{ij} = j \times p_i$, where i defines a portion, and j is the number of portions in the D_{OA} in each cycle of T-A-treatment. In our experiments j takes the value 2, 3, 4, 6 and 8. For each p_i, and each j value, we determined the number of the cycles required to complete the T-A-treatment. Consumption of oxidising agents and number of repeated cycles required for the end of treatment (organic matrix removed) determine the efficiency of the T-A-treatment.

The results indicate that the number of cycles decreases with increasing the number of portions of used oxidizing agents. Efficiency of treatment increases in order: $K_1=HNO_3 < K_3=HCl < K_2=H_2O_2$. The most effective treatment, with $K_2=H_2O_2$ as oxidizing agent, was obtained with 6 portions and in two cycles of T-A-treatment.

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F P10

Rehydration properties of vacuum dried strawberries infused with trehalose

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During processing, quality attributes of fruits may be lost or altered depending on the water content in the plant tissue. Dried and frozen strawberries, exhibit in particular severe damages of the tissue. Therefore, vacuum infusion has been used as pretreatment to drying and freezing of strawberries [1]. Vacuum impregnation (VI) at subatmospheric pressure for a short time allows an exchange of internal gas and liquid with an external solution through a hydrodynamic mechanism [2]. There is a big variety of additives and components that can improve the processing of fruits, but lately trehalose has lately gained more attention. The major application of trehalose is due to its natural function, mechanism of action and technical qualities [3].

In order to improve the quality of dehydrated strawberries, the influence of the infusion of calcium and trehalose on the retention of texture, color and anthocyanins content during dehydration of strawberry pieces was investigated. The 3 mm thick strawberry pieces were infused with 12 g/100 g trehalose solution and 2 g/100 g $CaCl_2$ solution under vacuum for 14 min. The fruits were vacuum dried at 60^{o}C for 2 h. Even though the color, flavor and taste of dried strawberry pieces are usually satisfactory, the collapse of the texture after rehydration limits their application in different food formulations. Water and milk at 4^{o}C and 50^{o}C and yogurt at 4^{o}C were used to rehydrate the dried strawberries. The mass transfer between the fruit pieces and the liquids during the rehydration process followed the exponential model. The physicochemical characteristics of the rehydrated products showed that the vacuum infused trehalose enhanced the retention of the anthocyanins and improved the texture in rehydrated strawberry pieces. The rehydration characteristics of the dried strawberry pieces were found to be influenced by the rehydration time and temperature as well as the choice of the rehydrating solution.

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F P11

Cellulolytic potencial of a strain *Paenibacillus* sp. isolated from soil

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Cellulases are the enzymes which cause hydrolyzis of the polysaccharide cellulose into smaller sugar units. Bacterial cellulases possess more advantages when compared to the cellulases from other sources. The gram positive, spore forming bacteria was isolated from soil. Strain was identified as *Paenibacillus chitinolyticus* after biochemical and 16S rRNA sequencing studies. The isolated strain was screened for cellulase activity by using a Gram's iodine metod on carboxymethyl cellulose (CMC) agar plate [1]. It has been found to produce cellulases which could liberate glucose from CMC (CMC-ase) and microcristalline cellulose Avicel (avicelase). The enzyme activity was measured by estimating the liberated reducing sugars using 3,5-dinitrosalicylic acid method [2].

A liquid medium containing 0.5% CMC and yeast extract proved to be a suitable carbon and nitrogen sources for cellulase production by the bacterium. Maximal cellulase production for CMC-ase 0.085 U/ml and for avicelase 0.17 U/ml was obtained after 48 h of incubation at 30 °C under aerobic conditions with 5% overnight culture and with addition of 0.5% CMC, 10 g/l yeast extract, $MgSO_4$ 0.5g/l, KCl 0.5g/l, $CaCl_2$ 0.02g/l and 1g/l Tween 80.

Paenibacillus sp. strain isolated from soil is available for further studies aiming the optimization of its cellulase production, facilitating its potential use in industrial applications.

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F P12

Fermentation of spent espresso coffee by *Hymenobacter psychrotolerans*

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Spent coffee grounds are produced during espresso coffee preparation. This waste coffee contains significant amounts of biologically valuable ingredients such as antioxidants. The effect of fermentation by *Hymenobacter psychrotolerans* on the antioxidant activities and total polyphenol content of the spent espresso coffee extract was determined.

Samples of spent espresso coffee were inoculated with selected natural strain of *Hymenobacter psychrotolerans.* The strains were cultivated on the carboxymethyl cellulose (CMC) broth and the supernatant was separated from the cells. Both supernatant and the cells suspended in saline were used for the treatment of samples. The solid state-fermentation was carried out at 30°C for five days. Solvent for extraction was water and the extracts were evaporated in the spray-dryer. The total polyphenol content was determined by the Folin-Ciocalteu method [1,2]. The antioxidant activity was determined using 2,2-diphenyl-1-picrylhydrazyl (DPPH) scavenging capacity, and Ferric Reducing Antioxidant Power (FRAP) methods [2,3]. Inhibition of DPPH radicals was expressed as IC_{50} value. Results were compared to those of non-fermented control sample. Fermentation of spent coffee with supernatant showed the increased content of polyphenols, while sample fermented with cells had the same amount of polyphenols compared to the control sample. IC_{50} values of fermented samples were lower compared to the control sample that indicates that fermented samples had higher antioxidant activity. The IC_{50} (μg/ml) values were 37.66, 29.00 and 18.57 for the control sample, sample treated with supernatant and fermented by cells, respectively. The FRAP assay shows that the antioxidant activity of the extract, compared to the control sample, increased only in the case of supernatant treatment, while the other extract had lower antioxidant activity. Fermentation of spent espresso coffee with *Hymenobacter psychrotolerans* have improved its antioxidative properties which present a potential for its application in pharmaceutical and food industry.

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F P13

The kinetic study of oleyl cinnamate synthesis

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Increased interest in phenolic acids stems from their physiological benefits, which make them very interesting for various applications in food and pharmaceutical industries [1]. The main advantage of phenolic compounds application as natural antioxidants instead of traditionally used synthetic ones, butylated hydroxytoluen (BHT) and butylated hydroxyanisole (BHA), is found in the fact that both BHT and BHA are potential carcinogens, hence their application continuously decreases [2]. On the other hand, one of the main obstacles for their utilization in foods and cosmetics is their low solubility in emulsions and oil-based formulas as repercussion of their hydrophilic nature. Introduction of aliphatic side chain groups via enzyme-catalyzed esterification, causing solubility alternations of phenolic acids, is an adequate way for increasing their industrial application potential [3]. The aim of this research was to enable efficient enzyme-catalyzed synthesis of liposoluble phenolic esters using synthesis oleyl cinnamate as model reaction and to determine kinetic constants which are very important for process scale up. Enzyme used for all esterifications is commercial preparation of lipase B from *Candida antarctica,* Novozyme 435. Initial kinetic study was performed in capped vessels where different concentrations of cinnamic acid (0.1-0.7 mol dm^{-3}), oleyl alcohol (0.1-0.7 mol dm^{-3}) and immobilized lipase (40 mg) were mixed in isooctane and put on orbital shaker set at 55°C and 150 rpm for 6 hours. Several different models were used to fit experimentally obtained data, but the best fit was obtained when ping-pong bi-bi model was used. Values of Michaelis Menten constants for cinnamic acid and oleyl alcohol and maximal velocity obtained by model are Km_c=0.64 mol dm^{-3}, Km_0=0.11 mol dm^{-3} and V_{max}=12 mmol dm^{-3} h^{-1} respectively.

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F P14

Production and characterization of extracellular α-galactosidase from *Aspergillus oryzae* DSM 1862

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The α-galactosidase is important industrial enzyme, used both in food and feed industry, that hydrolyses variety of non-digestible oligosaccharides with α-1,6-galactosydic bonds, thus allowing wider consumption of soybean-derived products [1,2]. The aim of this work was to produce this enzyme by submerged fermentation with *Aspergillus oryzae* DSM 1862 using several agricultural by-products (soybean meal, soybean flour, wheat bran, barley bran) as substrates. Soybean flour was proved to be the substrate of choice, being the most productive (3.34 IU/ml), and at the same time easiest for handling. In order to optimize cultural conditions for obtaining highly active preparations, different parameters were varied: substrate concentration (2-50 %), fermentation time (1-7 days), size of inoculum (0.5-5%). The highest activity was achieved after 6 days submerged fermentation using 2 % soybean flour and with 0.5 % of inoculum, since it showed no influence on produced activity. Furthermore, purification was performed by simple acetone precipitation and this was later proved by electrophoresis. The purified preparation was characterized, and it was concluded that optimal conditions for raffinose hydrolysis were 50 °C and pH 4.8.

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F P15

Oxidation kinetic of raspberry and blackberry seeds oils followed by DSC

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The oxidation of oils polyunsaturated fatty acids is the main reaction that affects the quality of the oil, and oil products during the storage and use. This reaction release heat that can be measured using differential scanning calorimetry (DSC). Thus, in recent times DSC is one of the most used technique to examine the oxidative stability of different types of oils. In this paper, using the isothermal and non-isothermal DSC, kinetic and thermodynamic parameters related to the oxidation process of oils obtained from raspberry and blackberry seeds was determined. Examined oils were obtained by hexane extraction of ground seeds. In isothermal DSC mode the oils were held at four different isothermal temperatures (110, 120, 130 and 140 ^{0}C) with oxygen flow through the DSC cell. The process of oil oxidation is manifested on the DSC curve in the form an exothermic heat flow appearing during initiation of the oxidation reaction. From resulting exotherm oxidation induction time (OIT) was determined (software TA Instruments Universal analysis 2000). The oxidation induction time is strongly dependent on the applied temperature. Based on the Arrhenius equation and activated complex theory following values were calculated: reaction rate constants (k = 1/OIT) at appropriate temperatures, activation energy (E_a) and pre-exponential factor (Z) from slope and intercept of the lines generated by regressing of ln *k* vs. $1/T_{iso}$; activation enthalpy ($\Delta H^{\ddagger}$) and activation entropy ($\Delta S^{\ddagger}$) from slope and intercept of the lines generated by regressing of $\ln(k/T_{iso})$ vs. $1/T_{iso}$. Obtained values for the oil from blackberry seeds are: k = $3{,}1*10^{-3}$ to $25{,}8*10^{-3}$ min^{-1}; E_a = 99,56 kJ/mol; $\Delta H^{\ddagger}$ = 96,21 kJ/mol; $\Delta S^{\ddagger}$ = -44,57 J/Kmol, while the corresponding values for the oil from raspberry seeds are: k = $9{,}4*10^{-3}$ to $97{,}7*10^{-3}$ min^{-1}; E_a = 101,94 kJ/mol; $\Delta H^{\ddagger}$ = 98,64 kJ/mol; $\Delta S^{\ddagger}$ = -29,42 J/Kmol. In non-isothermal DSC mode the oil samples were heated at different heating rates, β (2, 5, 7.5, 10, 15, 20 ^{0}C/min) in oxygen flow until the beginning of the oxidation process. Onset temperature (T_{on}) of oxidation was determined from the obtained DSC curves (software TA Instruments Universal analysis 2000). T_{on} at different heating rates were used to calculate the kinetic parameters of oil oxidation by Ozawa-Flynn-Wall (OFW) method. In this method, activation energy (E_a) and pre-exponential factor (Z) were calculated from the slope and intercept of lines generated by regressing $\log\beta$ vs. $1/T_{on}$. Based on the Arrhenius equation, reaction rate constant of oils oxidation was calculated at temperatures 25 and 200^{0}C. Obtained values for the oil from blackberry seeds are: E_a = 106,87 kJ/mol, Z = $6{,}8*10^{11}$ min^{-1}; k_{25} = $1{,}29*10^{-7}$ min^{-1}; k_{200} = 1,08 min^{-1}, while values for the oil from raspberry seeds are: E_a = 93,98 kJ/mol, Z = $6{,}2*10^{10}$ min^{-1}; k_{25} = $2{,}12*10^{-6}$ min^{-1}; k_{200} = 2,60 min^{-1}.Based on the obtained kinetic and thermodynamic parameters it can be concluded that the oil from raspberry seeds is more susceptible to oxidation then that oil from blackberry seeds.

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F P16

Pollutants emission during the printing on collagen casings for meat products

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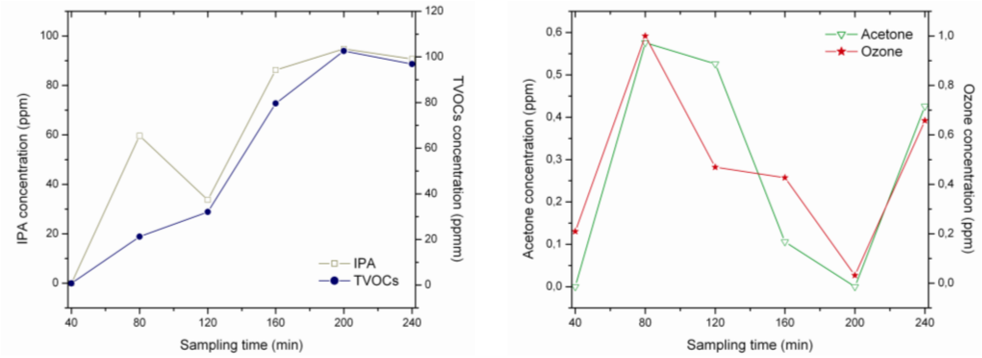
Primarily option of flexography is printing on flexible materials used in the meat, pharmaceutical, agricultural, chemical and cosmetics industry. The flexography printing release large amounts of volatile organic compounds (VOCs), which have caused concerns for health and safety, and contribute to the formation of ground-level ozone in indoor environment [1].

The objective of this study was to determine the presence of organic and inorganic air pollutants during the printing on collagen casings for meat products as well as to investigate the mutual correlation between them. The air samples were collected in a flexographic facility in Novi Sad by mobile gas chromatograph.

The mutual dependences of isopropyl alcohol (IPA), acetone, total VOCs (TVOCs) and ozone on sampling time were confirmed during the printing (Figure 1 a-b). The results shown that IPA and acetone had influence on the formation of ozone especially in time interval from start the production process to 120 minutes and after 200 minutes due to the intensive printing and longer retention of VOCs in indoor air.



a) b)

Figure 1. Dependence of IPA and TVOCs (a) and acetone and ozone (b) on sampling time

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F P17

Stabilization of w/o emulsions using polyglycerol esters as emulsifiers

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Double emulsions are complex liquid dispersion systems known also as “emulsions of emulsions”, in which the droplets of one dispersed liquid are further dispersed in another liquid. The inner dispersed droplets in the double emulsion are separated from the outer liquid phase by a layer of another phase [1, 2]. These multi compartment liquid dispersions have significant potential in many applications (pharmaceutical, cosmetic and food preparations), since the internal droplets can serve as an entrapping reservoir for active ingredients that can be released by a controlled transport mechanism. Most promising new application of double emulsions, as intermediate systems, is in preparation of solid or semi-solid micro-nano capsules.

The most common double emulsions are of w/o/w type, which are prepared by dispersing the w/o primary emulsion in water [3]. Even thaw w/o emulsions are very unstable systems thus have very limited application, for that reason the interest in their investigation increase in recent years. Obtaining a stable primary w/o emulsion is required as a first step in production w/o/w emulsions. Main factors affecting w/o emulsions stability are type of emulsifier, characteristics of water and oil phases, presence of electrolytes and polymers, etc. [4, 5].

The aim of this work is to investigate the possibility to obtain stabile 20% water in oil emulsions using different polyglycerol esters as emulsifiers (PGPR, Caprol 3GS, and Caprol 10G100). Triglycerides with middle length chains (caprilic/capric triglycerides) are used as the oil phase of emulsions. Investigation of droplet size and droplet size distribution and emulsions stability enable selection of emulsifier, or their mixture, for obtaining w/o emulsions with the best characteristics that may be used as the primary w/o emulsions for obtaining double w/o/w emulsion.

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F P18

Properties of o/w emulsions stabilized by gelatin/NaCN mixtures

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Emulsions are mixtures of two or more liquids that are normally immiscible. These systems are widely used for encapsulation, solubilization, entrapment and controlled delivery of active ingredients in food and pharmaceutical industry [1]. In order to answer the increasing demand for clean label excipients and natural ingredients, natural polymers can replace the potentially irritative synthetic surfactants used in emulsion formulation. All proteins and some polysaccharides are able to adsorb at the interface, thus decrease the interfacial tension and enhance the interfacial elasticity, resulting in emulsions stability. Potential interaction between used biopolymers can additionally improve emulsion stability [2, 3].

In the present study the ability of oppositely charged proteins, gelatin and NaCN, to stabilize o/w emulsions were investigated. In our previous studies interactions between these two proteins were investigated and complex formation was observed. Insoluble complex as a coacervate phase was formed at gelatin:NaCN ration 2:1. At all other rations soluble complexes were formed as a result of ionic interactions between proteins [4].

To investigate the ability of such complexes for emulsion stabilization 20% emulsions of medium chain triglycerides (MCT) in water were prepared. Stock emulsion (30%) of MCT oil in 1.7143% (w/w) gelatin solution were prepared by means of an Ultraturrax T-25 homogenizer. After that in 20g of stock emulsion 10g of NaCN of desired concentration was added during midle stirring on macnetic stirrer. Concentrations of added NaCN were 0.05; 0.1; 0.15; 0.5; 1.5; 2 and 3% (w/w) of NaCN in final emulsion. So, final emulsion was composed of 20% MCT oil in mixture of 1% (w/w) gelatin and various NaCN concentrations. Size and particle size of stock emulsion was determined. Stability and zeta potential of final emulsions were determined, and detailed rheological investigations were performed.

These investigations showd an influence of interaction between proteins on emulsion stability inducing diferent type of phase separation in emulsions with NaCN concentrations corresponding to the region before insoluble complex formation comparing with those with NaCN concentrations after complex dissolution. Also, there was significant change in zeta potential with increasing NaCN concentrations. Influence of gelatin/NaCN interactions on emulsions properties was confirmed by rheological investigations. Sauch interations make an influence on flow behavior and viscoelastic properties of emulsions as well.

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F P19

Total antioxidative capacity of some honey bee pollen collected in serbia

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The first paper on the implementation of pollen as a food display Meehan in 1873 [1]. While honey is the main energy substance for bee, pollen is the main nutrient that contains high amounts of protein, minerals, carbohydrates, fats, polyphenols and other substances. Only in the case of unifloral pollen can claim with absolute certainty that there is continuity in the chemical composition of which is of great importance for its use in medicine and nutritional supplement [1]. The antioxidant properties of substances primarily based on their ability to neutralize free radicals, which may be present in the body and as such cause different types of disease (especially cancer), or lead to the death of aging cells. Based on previous researches it was found that strong antioxidative capacity in bee pollen has been showed by different polyphenolic substances, such as flavonoids [2]. Due to the difficulties in measuring individual antioxidant components of a complex mixture, their activity is expressed as total antioxidative capacity. Our findings showed that such testing hasn't been done for honey bee pollen in Serbia.

In the present study, total antioxidative capacity of 27 honey bee pollen samples collected in different regions of Serbia were investigated according to the procedure proposed by Serpen [3]. The obtained results are expressed as mmol TROLOX/kg of dried pollen samples. They indicated that there is a significant differences in antioxidative capacity of investigated honey bee pollen samples. The lowest value for the antioxidative capacity have showed in samples 4 (27.46). On the other hand, the greatest antioxidant capacity were determinate in sample 12 (138.89). Sample 4 was collected in Belgrade, while sample 12 was collected in Mala Krsna. It could be noted that the samples were of different geographical origin and that the maximum value was 5 times higher than the minimum. Based on the obtained results it could be concluded that the geographic origin could have an impact on the content of phenolic compounds. Several factors, such as reaction parameters and heterogenity of pollen sample, also, could have an impact on the results. It should be pointed that there are some other substances present in pollen that could contribute to its total antioxidative capacity which will be investigated in our further researches.

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Characteristics of supreme inbreed and hybrid lines of maize

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Intensive studies and the development of maize inbred lines with erect top leaves were carried out with following results: non-invasive photosynthetic fluorescence method can be applied in breeding and the maize hybrid seed production and that the estimation of prestigious maize inbred lines for their resistance and adaptability to increased and high temperatures, as well as, to drought, can be performed. The application of the stated method provided the determination of many properties and parameters of photosynthetic apparatus of observed prestigious maize inbred lines with erect top leaves:

- -Temperatures at which smaller or greater conformational and functional changes in the thylakoid membrane occur,
- -Values of activation energies (Ea, kJ mol^{-1}) along straight lines before and after the occurrence of critical temperatures in the thermal process,
- -Different monotony of the increasing part of the thermal curve, which points out to uneven resistance and adaptability to increased and high temperatures, as well as, to drought,
- -It was shown that observed inbred lines have a trait of the erect position of top leaves and a greater dry down rate in the grain maturation period.

The following relevant properties of maize hybrids, developed from the stated maize inbred lines with erect top leaves, were analysed: dependence of their yields on the crop density and quality of commercial maize of observed maize hybrids. It was presented that observed maize hybrids tolerated crop densities up to 70,000 plants ha^{-1}. It was shown that commercial maize of observed maize hybrids with erect top leaves was of exceptional quality that provided its diversified utilisation.

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F P21

Lipase-catalyzed synthesis of phloridzin esters

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Phloridzin is member of chemical class of dihydrochalcones, phenylpropanoids with structure similar to chalcones, immediate flavonoid precursors, hence it is often classified as flavonoid glucoside [1,2]. It is usually extracted from *Malus* species since it is very abundant in young apple leaves and twigs. Due to its phenolic structure, phloridzin has significant antioxidant activity and anti-UV properties, which makes it interesting for application in food and cosmetics. Major limitation to wider application of phloridzin is its low solubility in hydrophobic environment, which can be circumvented by synthesis of physiologically active compounds derivatives by acylation of phloridzin. Synthesis of acyl esters can be catalyzed by inorganic catalysts or enzymes, but chemical esterification is not regioselective and results with unwanted functionalization of phenolic hydroxyl groups responsible for antioxidative properties.

Therefore, in our study enzymatic esterification of phloridzin was performed using immobilized lipase from *Candida antarctica* (Novozyme® 435). Several organic solvents were tested and acetonitrile was proved to be the most adequate medium for this reaction. Different acyl-donors were used with respect to chain length and saturation level. Potential physiological activity of obtained esters was evaluated by determination of their antioxidant activity using DPPH assay, so acyl donors were compared with respect to both, product yields and antioxidant activity. After comparison of results of preliminary study, phloridzyl oleate was selected as derivative with the best prospects and it used in further experimental series for optimization of key experimental factors. Response surface methodology was applied as statistical tool for optimization of product concentration (in mM) as output and analyzed factors were: reaction time, temperature, enzyme concentration, substrate molar ratio, and phloridzin concentration. After statistical analysis each of examined experimental factors was found significant and second order regression model was obtained. It was established that highest product concentration can be expected at 68 °C, with 0.17 M of phloridzin, 2,5 % (w/v) of enzyme, 19-fold molar excess of oleic acid after 7 days of reaction.

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F P22

A comparison of maize hybrids for yield, carbohydrates and *in vitro* digestibility

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Maize is one of the most important and widely grown crops produced in the world. In Serbia, maize has been traditionally cultivated as a number one field crop. The main aim of modern maize breeding is development of high yielding hybrids tolerant to drought and pests. Little attention has been paid to the nutritional value of maize as a food and feed row material. However, advances have been made by breeders within this area as well, resulting in maize hybrids with specific traits.

The objective of the present study was to investigate and compare six maize hybrids of a different genetic background developed at the Maize Research Institute, Zemun Polje, Belgrade, Serbia, for yield, carbohydrates and *in vitro* digestibility. The selected hybrids were sown in 2012. The kernel chemical composition (content of starch, protein, oil, crude fibre and ash) and amylase and amylopectin contents in starch were determined in samples of observed ZP maize hybrids. In addition, the following traits were determined: biomass yield and lignocellulose fibres (NDF-neutral detergent fibres, ADF-acid detergent fibres, ADL-acid detergent lignin, hemicellulose and cellulose), as well as dry matter digestibility (IVTD-*in vitro* true digestibility) of whole maize plants.

Obtained results point out that six investigated ZP maize hybrids had different kernel chemical compositions, especially in the starch as its major constitutional componet. The content of amylose and amylopectin in these starches is characteristic for normal maize starches. The dry matter yield of the whole plant and the yield of digestible dry matter of the whole plant varied from 9.4 (ZP 341) to 13.2 tha^{-1} (ZP 758) and 5.9 (ZP 341) to 8.6 tha^{-1} (ZP 427), respectively. The NDF, ADF, ADL, hemicellulose and cellulose contents of the whole maize plant varied from 48.07 (ZP 427) to 56.89% (ZP 802), 22.23 (ZP 648) to 26.54% (ZP 802), 1.42 (ZP 666) to 2.21% (ZP 802), 24.63 (ZP 427) to 30.35% (ZP 802) and 20.78 (ZP 648) to 24.45% (ZP 341), respectively. The lignin NDF ratio (L NDF^{-1}) of observed maize hybrids ranged from 30 (ZP 684) to 39 g kg^{-1} (ZP 758 and ZP 802). The dry matter digestibility of the whole plant ranged from 56.67 (ZP 802) to 67.34% (ZP 648) with the NDFD (NDF digestibility) calculated by the equation: NDFD=100((NDF-(100-IVTD))/NDF) varying from 166 (ZP 758) to 322 (ZP 648) g kg^{-1}.

Results gained in this study show that six investigated ZP maize hybrids varied in the kernel chemical composition, dry matter yield, lignocellulose fibres components and dry matter digestibility of the whole plant and point out to the great importance and necessity of the characterisation of the released maize hybrids, as well as, of the determination of parameters affecting its utilisation value. This range of maize quality parameters offers a broad possibility in hybrid selection for new specific uses of maize for food and feed.

F P23

Study of antioxidant activity of some seeds extracts by EPR and DPPH spectrophotometric methods

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The antioxidant activity of extracts from the seeds of *Vitis vinifera* L. (grapes, *Vitaceae*), *Citrullus lanatus* (Thunb.) Matsum. & Nakai (watermelon, *Cucurbitaceae*), *Citrus limon* (L.) Burm.f. (lemon, *Rutaceae*), *Citrus* x *paradisi* Macfad. (grapefruit, *Rutaceae*) was investigated. The extracts were realized by reflux in 96% ethanol for 1 hour.

For electronic paramagnetic resonance (EPR) analysis, an aliquot of each ethanolic extracts was evaporated at room temperature. The dry residue was extracted in chloroform and the obtained mixture was filtered. The decrease of peak height of free stable radical 2,2-diphenyl-1-picryl hydrazyl (DPPH) radical, as a result of its interaction with antioxidants present in the extracts in time, was measured [1].

DPPH free radical scavenging activity, total phenols (TP) and flavonoids contents of ethanolic extracts were determined spectrophotometrically [2].

The antioxidant activity of seeds extracts determined spectrophotometrically was expressed in terms of Trolox equivalents and varied as follows: 0.327 ± 0.031 for lemon, 0.352 ± 0.027 for grapefruit, 0.713 ± 0.0064 for watermelon and 56.6 ± 3.5 for grapes g/100 g dry weight (dw). A comparison between the antioxidant activities analyzed by the two methods was performed. The results were confirmed by the ones of TP and flavonoids content. Thus, values of TP content were varied between 0.0542 ± 0.0021 (for grapefruit seeds extract) and 4.14 ± 0.072 (for grape seeds extract) g equivalents of gallic acid/100 g dw and values of flavonoids content were between 0.0533 ± 0.0066 (for grapefruit seeds extract) and 0.195 ± 0.023 (for grape seeds extract) g equivalents of quercetin/100 g dw. Of all analyzed extracts the grape seeds extract is the richest in polyphenols and has the highest antioxidant activity.

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F P24

A multiple element analysis of a food by ed-xrf: mussels as a case study

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A relatively new analytical method X-ray fluorescence (XRF) has been developed and shown capability of trace element analyses mainly in environmental samples. ED-XRF was used for the simultaneous determination of essential, neutral and toxic elements in the mussel *M. galloprovincialis* in two seasons, fall and spring from the southeastern Adriatic coast, Montenegro. Results showed that the mussel tissue contains As, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Hg, Fe, I, K, Mn, Ni, P, Pb, Rb, S, Sb, Si, Sn, Sr, Th, Ti, V, Zn, and Zr. Generally, Cr, Si, V and Ti concentrations in mussels from both seasons were the same and concentrations of essential (Ca, Cl, Cu, I, Fe, K, P, S, and Zn) and toxic (Hg, Cd, Pb, and As) elements were much higher in the fall mussel samples.

The results observed the presence of significant quantities of the essential elements (Ca, Cl, Co, Cr, Cu, I, Fe, K, Ni, P, S, Si, Zn, and V) in mussels. They can be considered as a good source of trace elements supplementation to human body by their usage in certain amounts. The recommended dietary allowance (RDA) of essential elements and the provisional tolerable weekly intake (PTWI) of toxic elements were estimated.

As the method of non-destructive nature, this multi-element analytical procedure can provide new potential method for detecting trace elements in foods and in many agricultural commodities. Practical application of ED-XRF method analyses can include food control and safety on a number of elements, as well as for evaluating environmental impact derived from current aqua and agriculture practices.

F P25

Pectins determination in juice, pulp and whole fruits of strawberry, raspberry and blackberry of the West-Serbian origin

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Strawberry (*fragaria versa, fragaria ananassa*), raspberry (*rubus idaeus*) and blackberry (*eubatus focke*) are season berries well known as health benefit fruits.

In this paper the total level of pectin's in berries of the West-Serbian origin (strawberry, raspberry and blackberry) as well as in their particular parts (juice and pulp) is presented. Pectin level in berry fruits is very important for further processing and jellies and jam production. Methods applied for extraction, isolation, separation, characterization and quantification of phytochemicals are different. The methods of extraction are especially chosen with a minimum of polyphenols degradation, *i.e.* to obtain them in a native condition like they are found in berries. The berries were firstly frozen for storage, and then spontaneously defrosted before each analysis. An aliquot of berries was taken away to separate the juice and pulp by pressing and centrifugation. The total pectin's were determined according to the gravimetric method described in Manual of analysis of fruit and vegetable products and the yield of pectin's was expressed as calcium pectate. It was found, that all berries showed the similar pectin content. Concerning the particular parts of berries, the strawberry pulp keeps the largest amount of pectins (1.24%), followed by blackberry (0.96%) and raspberry (0.89%), whereas the total pectins in all of three berries slightly differ (strawberry 0.68%, blackberry 0.65% and raspberry 0.66%). The juices of berries were found to have very low content of pectins (0.10 – 0.15%).

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F P26

Variations of some antioxidants in soybean grain affected by foliar fertilizers

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Nutritive value of soybean grain could be increased with foliar fertilizers by alteration of its chemical composition, particularly antioxidants. The trial included application of different organic fertilizers: Eko-fert, Zlatno inje (both are organic fertilizers), Lithovit forte (CO_2 foliar fertilizer), Agrostemin zlatni (based on plant extracts, consisting of amino acids, organic acids and phytohormone inhibitors), Bioplant Flora (organic fertilizer with humic acids and microelements), Algaren BZn (organic fertilizer based on *Ecklonia maxima* algae extract with addition of B and Zn), Zircon (based on phenolic acids, identically to *Echinacea purpurea* L. extract), as well as phytohormone preparation Epin extra (based on 2,4-epibrassinolide), which were applied at the beginning of flowering (first half of June of 2012) on two soybean varieties, Nena (standard variety) and Laura (variety lacking in Kunitz trypsin inhibitor). Experiment was provided in rain-fed conditions on chernozem soil type at the vicinity of Zemun Polje. Contents of different antioxidants in grain, after harvesting were followed: total glutathione, total phenolics, phytate, β-carotene, as well as elements, Mg and Zn.

The highest average grain yield and 1000 grain weight were achieved in Zircon treatment. This treatment had also the highest impact on Mg accumulation. Lithovit forte, as fertilizer which enables effective CO_2 usage, increased in the highest extent content of the most important antioxidants in soybean grain, total glutathione and phenolics, as well as Zn. On the other hand, Agrostemin zlatni, as mixture of plant extracts with inhibitors had the highest impact on phytate and β-carotene content, together with the lowest content of Mg and Zn, among all treatments. The positive impact of Eko-fert fertilizer was reflected through increased content of glutathione and β-carotene and the lowest content of phytate, which was also considered as anti-nutrient, among all applied treatments.

The regression analysis emphasized high and positive correlation between 1000 grain weight and Zn content ($R^2 = 0.533$), as well as high and negative correlation between 1000 grain weight and glutathione content ($R^2 = 0.466$) and phenolics ($R^2 = 0.343$), indicating that grains with better filling (higher weight) have possible higher Zn and lower content of glutathione and phenolics. Irrespective to fact that variety Nena had higher average contents of all examined antioxidants, giving it advantage as high yielding variety, with higher content of antioxidants. Laura showed higher reaction to all applied foliar fertilizers, increasing the average content of glutathione, phenolics and β-carotene. This fact gives the significance to application of foliar fertilizer with aim to increase nutritive value of variety which primary has high nutritive value owing to absence of Kunitz trypsin inhibitor.

F P27

Total polyphenol, flavonoid contenc and antioxidant capacity of commercially avaiable black, green and herbal tea infusions

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Tea is an aromatic beverage commonly prepared by pouring hot or boiling water over cured leaves of the tea plant, *Camellia sinensis*. After water, tea is the most widely consumed beverage in the world. Tea has historically been promoted for having a variety of positive health benefits, and recent human studies suggest that green tea may help reduce the risk of cardiovascular disease and some forms of cancer, promote oral health, reduce blood pressure, help with weight control, improve antibacterial and antivirasic activity, provide protection from solar ultraviolet light, increase bone mineral density, and have anti-fibrotic properties, and neuroprotective power.

The objective of our research was to evaluate the total polyphenol and flavonoid contents as well as antioxidant activity of black tea, green tea and thirteen herbal tea samples from Serbian markets. Total polyphenol content was determined spectrphotometrically according to the Folin-Ciocalteu method (λ=760 nm) [1], using gallic acid (GA) as a standard, and ranged from 240.73 mg/g (green tea) to 26.16 mg/g (nettle). The total flavonoid content in selected tea samples was determined according the aluminum chloride spectrophotometric method (λ=510 nm) [2]. Catechin was chosen as a standard and the results expressed in milligram catechin equivalents per gram of tea extract (mg CE/g). Results are ranged from 84.94 mg/g (green tea) to 12.54 mg/g (nettle). DPPH radical scavenging activity, 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) radical cation scavenging activity (ABTS), ferric reducing-antioxidant power (FRAP) and reducing power assay Fe(III) to Fe(II) (RP) were used to assess the antioxidant capacity (AC) of herbal teas. All samples showed antioxidant power, but a wide range of ACs was observed. Obtained results suggested that FRAP and Fe(III)/Fe(III) method correlated strongly with the total phenolics content ($R^2 = 0.92246$, $R^2 = 0.88084$, $p < 0.0001$). Antioxidant power of green tea and bearberry tea is considerably higher than black tea.

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F P28

Mathematical models of water loss and solid gain
during osmotic treatment of pork meat in sugar beet molasses

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The main objective of this work was the investigation of several models: diffusive, Azuara's Peleg's, second order polynomial and an exponential (Weibull-type) model on the mathematical modeling of water loss and solid gain by pork meat cubes (*M. triceps brachii*) immersed in sugar beet molasses solutions, during osmotic treatment process. Experimental design allowed to access the effect of molasses solution concentration (concentrated at 60-80% w/w), temperature (20, 35 and 50^{o}C) and immersion time (1-5h), and to quantify water and solid mass transfer coefficients. The considered empirical models were able to represent satisfactorily the transfers of water and solids during all osmotic treatments, and Peleg's model was used to predict the equilibrium condition used for diffusive model.

The huge difference in osmotic pressure between hypertonic solution and the immersed meat tissue, causes the vast initial loss of the water and solid gain at the beginning of the dehydration process. The maximum value of water loss (0.58 g/g i.s.w.) was achieved, after 5 hours, at maximum concentration of 80% w/w, at 50^{o}C temperature. The aim of osmotic dehydration is the achievement of as low as possible solid uptake, and the most acceptable results were achieved by using sugar beet molasses concentrated to 80% w/w (0.17 g/g i.s.w.), after 3 hours of osmotic process.

The diffusive model was able to represent well both water loss and solid gain rates, using a single parameter (represented as apparent diffusion coefficient).

Mass transffer coefficients, for both solid and water, rise with an augment in osmotic solution concentration, while increase of the concentration have lead to the decrease of activation energy for both water and solids transfer. The highest diffusion coefficient for transport of water observed was $1.48 \cdot 10^{-9}$ m^2/s, and $1.28 \cdot 10^{-9}$ m^2/s for transport of solids, both recorded at temperature of 50 °C and sugar beet molasses solutions concentration of 80 %. The maximum of activation energies were reached at 20 °C, 85.338 kJ/mol for water transport, and 84.919 kJ/mol for solid transport.

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F P29

Macro elements composition of the osmotically dehydrated fish meat

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Sugar beet molasses is being used as osmotic dehydration (OD) solution, primarily due to the high dry matter content (80%) and specific nutrient content [1]. Minerals and vitamins from sugar beet molasses, penetrate from hypertonic solution into the meat tissue and enrich the food material. Differences of macro elements content in fish meat are mainly determinated by food processing. [1-3]. Macro elements composition of the raw fish meat (*Carasius Carasius*) and osmotic dehydrated fish meat in the solution of sugar beet molasses were investigated.

Dry matter content of the samples was determined at 105°C in a laboratory oven until constant mass. The combination of thermal treatment at 350°C, and wet acidic treatment at 160°C was used for samples preparation. The dry samples were processed for minerals determination by wet digestion, approximately 2 g each, transferred to vessels, and afterwards 4.5 ml 65% HNO_3 and 10.5 ml 35% HCl were added. The treatments were repeated to obtain the white sediments that were dissolved in 0.07M HNO_3. The content of metals present in the corresponding solutions was determined by inductively coupled plasma optic emission spectrometry (ICP-OES). ICP-OES measurement was performed using Thermo Scientific ICAP 6500 Duo ICP (Thermo Fisher Scientific, Cambridge, United Kingdom) spectrometer equipped with RACID86 Charge Injector Device (CID) detector, standard glass concentric nebulizer, quartz torch, and alumina injector. Samples were analyzed in triplicate.

Results suggests that sugar beet molasses solution affects treated fish meat samples concerning concentration of macro elements. Content of macro elements in the osmotic dehydrated fish meat, compared to the content obtained for the raw fish meat, shows a significant increase of Na and K cations - 3.5 and 2 times, respectively. On the contrary, contents of Ca and Mg cations in OD fish meat decreased 2 and 1.5 times, respectively.

The results show that osmotic dehydration process of *Carasius Carasius* fish meat by sugar beet molasses significantly influences the content of investigated macro elements

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F P30

Effect of prebiotic, probiotic and synbiotic suplementation on the quality of cookies

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The importance of consuming prebiotic, probiotic, and synbiotic foods for improvement of the quality of life is clearly described in the scientific literature, and the number of foods to which they can be applied is increasing [1-3]. Hence, the development of such products is becoming priority for both science and food industry.

The prebiotics (galactooligosaccharides), probiotics (*Lactobacillus acidophilus* Rosell-52, *Lactobacillus rhamnosus* Rosell-11 and *Bifidobacterium longum* Rosell-175) and their combination as synbiotics were added to cookies and their effect on the textural properties, color changes and consumer acceptability was evaluated. Texture profile was evaluated on texture analyzer using the compression test. The L*, a* and b* color values were recorded and used to calculate the browning index and total color change. The results showed that texture was better maintained in cookies with prebiotic and probiotic. Addition of prebiotic and probiotic to cookies resulted in harder samples with darker color. To study the joint variability of the attributes for which significant differences were found, principal component analysis was applied to average scores of all parameters. In addition, the quality and stability (shelf life) of cookies supplemeted with prebiotic, probiotic and synbiotic during three months storage was evaluated. The analysis showed that all cookie samples were stabile and their quality acceptable. All samples sets contained 10^8 cfu/g over the test period, which is sufficient for a probiotic effect, and is comparable to counts of probiotic bacteria in commercially available dairy products.

Sensory analysis represents a very important step in assessment of all kind of food products. The choice of the appropriate sensory technique allows obtaining relevant information on the consumer acceptance [4]. The majority of consumers (89.6%) rated the cookies with prebiotic higher than the probiotic and synbiotic cookies for taste, color, flavor, texture, and overall acceptability. The information acquired is of great interest for further development of the products whose nutritional and sensory characteristics will meet consumer demands.

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F P31

Screening for factors affecting dextransucrase production from *Leuconostoc mesenteroides* isolated from water kefir grains using statistical approach

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A leuconostoc strain was isolated from water kefir grains obtained from a household in Belgrade, Serbia. Strain was identified as *Leuconostoc mesenteroides* after biochemical and 16S rRNA sequencing studies. The isolated strain was found to produce dextransucrase. Culture medium and growth conditions for enzyme production were screened and optimized using the statistical design technique of Plackett-Burman [1]. Plackett-Burman design with variables viz. sucrose, yeast extract, beef extract, K_2HPO_4, Tween 80, incubation time, temperature and inoculum, was performed to screen main factors affecting enzyme production. Based on factorial design seventeen experiments were performed. Each factor was examined at two levels: -1 for low level and +1 for high level, and five center points were run to evaluate the linear and curvature effects of the variables.

The enzyme activity was measured by estimating the liberated reducing sugars using 3,5-dinitrosalicylic acid method [2].

Among tested factors positive effect gave K_2HPO_4, Tween 80 and sucrose. Dextransucrase activity varied from 0.52 to 4.81 U/ml. Maximum activity was acquired from medium contained 50 g/l sucrose, 10 g/l yeast extract, 15 g/l beef extract , 60 g/l K_2HPO_4, 2g/l Tween 80, inoculated with 2% overnight culture and cultivated at 23^{o}C for 16h.

The resultats from statistical design technique of Plackett-Burman show that tested strain has high potential for dextransucrase production. Further optimization with positive factors should be done by the other statistical design technique, response surface methodology.

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F P32

Adsorption of green tea polyphenols onto spent coffee grounds

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Some waste materials demonstrated considerable adsorption affinity for phenolic compounds. This property serves two purposes: the recovery and purification of bioactive compounds or fractions from plants, as well as treatment of wastewaters that are leaden by phenolics. This work presented the processing of solutions containing polyphenols by adsorption-desorption studies using spent coffee grounds. As a model system, green tea aqueous extract was prepared. The experiments were performed by batch sorption on a rotary shaker and dynamic column studies. 2 g of spent coffee sample was contacted with 100 ml of green tea extract solution for a predetermined period of time. The results were expressed as the residual total polyphenol concentration of tea extract, measured by the Folin - Ciocalteu method. Batch sorption studies showed a faster removal affinity, compared to column performance. After just 30 min of contact time, the removal percent of tea polyphenols by coffee residues amounted 40%. The desorption studies were also performed, and the results lead to effective purifying and concentrating of tea polyphenols for its further use.

As this study investigated the adsorbent capacity of no-cost waste material, such as spent coffee, for phenolic compounds binding, the obtained results were noticeable and offered numerous opportunities for a further experiments in this field.

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F P33

Enzymatic hydrolysis of egg-white proteins in a membrane reactor

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The objective of this research was to improve antioxidative properties of egg-white proteins by means of enzymatic hydrolysis. For this purpose a continuous stirred tank reactor including polyethersulfone ultrafiltration module with a molecular weight cut-off of 10 kDa was employed. Several proteolytic enzymes have been tested in order to obtain best quality of peptide-based formulations intended for human consumption. Amongst protease form *Bacillus licheniformis* (Alcalase), protease form *Bacillus amyloliquefaciens* (Neutrase) and protease from papaya latex (papain), the highest degree of hydrolysis (DH), as well as the best antioxidative properties of obtained hydrolysates, were achieved with Alcalase. Further optimization included finding of the optimal enzyme concentration and residence time. Results showed that the DH was directly dependent upon the enzyme concentration, while the permeate flow did not show any influence on the DH. The reactor was maintained in operation for 3 h at 50 °C and pH 8 with permeate flow of 2 cm^3 min^{-1}. Degree of hydrolysis reached steady value of 60 % after 75 min. Antioxidative properties were analyzed with DPPH method and confirmed with cyclic voltammetry. Results undoubtedly show that the obtained products have improved antioxidative properties compared to untreated egg-white proteins.

F P34

Chemical modification of Purolite A109 for application in lipase immobilization

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Modern industry recognizes enzymes as important catalysts for batch production of food, drugs and cosmetics. Because of their price and poor technical characteristics in free form, enzymes are mostly used as immobilized derivative. Therefore, there is a constant need for new and improved supports, possessing sufficient amount of active groups on it's surface to interact with enzyme, but on the other side chemically inert to the reaction media. Mechanical stability and price range are as much important as chemical stability.

The aim of this study was to investigate properties of modified ionic resin Purolite A109 for lipase immobilization. Purolite A109 is polystyrenic (styrene-divinylbenzene copolymer), macro porous anion exchange resin with primary amine weak base functional groups. It's advantages could be low price, and excellent mechanical and chemical characteristics. Modification of this resin was performed using cyanuric chloride (CTC) and epychlorhydrine. In both cases FTIR spectroscopy confirmed that modification process was successful. Lipase from *Candida rugosa* was immobilized on both modified supports. Approximately 30% of proteins was bound to both carrier. Hydrolytic activity of both, free and immobilized lipase was determined, and based on these results activity retention after immobilization process was calculated. Results showed that significantly higher activity retention was obtained in case of CTC-Purolite – 67 %. Thermal stabilities of these two immobilized enzymes on 65 °C were compared to thermal stability of free enzyme. Relative activity of free enzyme decreased below 50% of initial activity within 30 min. On the other hand, both immobilized enzymes showed significant thermal stability. Relative activity of epoxy-Purolite dropped below 50 % of initial activity within 3 hours, while CTC-Purolite dropped below 50 % of initial activity within 5 hours.

F P35

Thermal analysis of the mollases used for meat osmotic dehidratation

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Molasses, a by product of sugar manifacture, mainly consists of water 17–25g per 100 g weight, 30–40g sucrose, 4–9g glucose, 5–12g fructose, polysaccharides: dextrin, pentosans, polyuronic acids 2–5g, and inorganics. Molasses is, industrially important, and this can be enhanced with understanding of its physical properties, amongst others, to assist its handling, processing, quality, storage and beter performance in the process of osmotic dehidratation. Also, molasses has been well known of its health benefits as it provides for excellent source of the nutrients [1]. In this work thermal characteristics, by the maeans of differential scanning calorimetry (DSC) and modulated differential scanning calorimetry (MDSC), of molasses, used for osmotical dehidratation of pork meat, has been studied in the aime of beter understanding of molasses glass transition fenomena. Seven samples of molasses, obtained from three Serbian sugar mills with different water content, before and after osmotic dehidratation and one sample of dried mollasses, has been studied by DSC in the cyclic heat-cool-heat scans, in the temperature range from -90 ^{0}C to 90 ^{0}C, heating rate Hr=10^{0}C/min and cooling rate Cr=5^{0}C/min, N_2 purge flow of 50 ml/min. MDSC cyclic heat-cool-heat scans were conducted in temperature range from -90 ^{0}C to 90 ^{0}C, with heating rate Hr=5 ^{0}C/min with modulation of ±0.80 ^{0}C amplitude and 60s period of modulation, under N_2 purge flow of 50 ml/min. Moisture was determined by standard method JUS ISO 1442: 1997. Al scans were performed on the DSC Q1000 calorimeter**,** TA Instruments**,** DE, USA. The Universal Analysis^{TM} software was used to obtain the glass transition parameters (onset, $T_{onset;}$ midpoint, T_g; final T_{end}, and the shift in specific heat capacity (ΔCp)). From results obtained it was found that there was strict dependence between water content and molases glass transition (T_g) temperature what is in agreement with literature [2]. The transition temperatures (midpoint), T_g, ranged from -54.3^{0}C to -32.1^{0}C, while the change in heat capacity (ΔCp) was from 1.1 to 2.4 J/g/1^{0}C. Dried mollasses T_g was fuond to bee -33.0 ^{0}C, which is in agreement with results obtained by Fox model for glass transition prediction and predicted T_g of the anhydrous molasses [1]. Highest moisture, sample showed the lowest glass transition temperatures, while the highest glass transition temperatures were obtained with sample, which is the driest of the molasses. Using MDSC, the reversing and nonreversing thermal events in the low temperature region of molasses have been obtained, suggesting on one thermal processes.

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F P36

The Presence od residues of certain pharmacologically active substances in veterinary drugs in raw milk from Montenegro area

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For the safety of food of animal origin it is especially important to use drugs in the treatment and control of animal health and thus the validity of the obtained products. This paper deals with the presence of residues of certain pharmacologically active substances of veterinary drugs. The analysis of raw milk samples was conducted from three different locations in Montenegro with the aim of determining residues of veterinary drugs in the sample. Penicillin G, Amoxicillin, Oxacillin and Chloramphenicol were determined. The analysis was conducted on liquid chromatography mass. The obtained results indicate the presence of residues of these drugs, but to the extent which is below the maximum allowable concentration (Regulations on Maximum Allowable Concentrations of Residues of Pharmacologically Active Substances of Veterinary Drugs in Foods of Animal Origin, Official Gazette of the Republic of Montenegro No. 51/2007). Therefore, from the standpoint of food safety, the use of the analyzed raw milk can be considered safe.

F P37

Optimization RP-HPLC method for determination some bioflavonoids in *Brassica oleracea* species and their antioxidative activity

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Rapid RP-HPLC method with UV (DAD) detection for simultaneous quantification of bioflavonoids quercetin, apigenin, catechin, epicatechin, kaempferol and luteolin in some food samples (cauliflower, broccoli and brussels sprouts Brassica oleracea species) was developed with the aid of LC-Simulator (ACD Labs® suite) software.

The extracts of food samples obtained either by Soxhlet, ultrasonic extraction, maceration or water extraction were analyzed for bioflavonoid content using standard addition method. The optimized separation was achieved on Hypersil GOLD aQ column with isocratic elution and mobile phase composition A: 2 % acetic acid in water and B: acetonitrile. R_s values were in the range from 1.3 to 3.1, indicating good selectivity of the method. The obtained results (mg/100 g fresh weight) for different bioflavonids were for quercetin in the range 0.64 – 0.90, 0.54 – 0.71, 0.45 – 0.69, kaempferol in the range 0.62 – 0.80, 0.52 – 0.71, 0.43 – 0.71, catechin in the range 0.31 – 0.52, 0.16 – 0.58, 0.23 – 0.48, luteolin in the range 0.26 – 0.43, 0.11 – 0.27, 0.16 – 0.30, apigenin in the range 0.09 – 0.18, 0.12 – 0.23, 0.08 – 0.19 and epicatechin in the range 0.25 – 0.41, 0.15 – 0.31, 0.23 – 0.38 for cauliflower, broccoli and brussel sprouts samples, respectively and generally show good agreement with published data. Low detection limits (0.014 – 0.063 μg/mL) were obtained with acceptable recoveries (90 – 109 %). Total time of analysis was less than 11 min, therefore the proposed method represents significant improvement over existing methods.

Extracts from Brassica vegetables, obtained using different extraction procedure, were studied for their radical scavenging effects. Radical-scavenging activity was measured by UV/Vis spectrophotometry using stable 1,1-diphenzl-2-picrylhydrazyl (DPPH) radical. Fresh Brassica had the antioxidant activity almost two times higher than frozen samples. Scavenging of DPPH showed second-order kinetics at the beginning of the assay period and later the first-order one. Different kinetics suggested the presence of polymerized and/or less active antioxidants with different scavenging mechanisms for particular polyphenolic compounds.

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F P38

Evaluation of nutritional value of soybean okara produced by hydrothermal cooking

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Raw okara, also called “soy pulp” is a byproduct of the soymilk industry. It is a white-yellowish material consisting of the insoluble parts of the soybean seeds which remains in the filter sack when pureed soybeans are filtered for the production of soymilk [1]. High protein content of around 30% (31.81-40.36% on dry basis) [2] makes okara a potential source of low cost plant protein for human nutrition. Moreover, the ratio of essential amino acid to total amino acids in okara is similar as in soymilk and tofu [3]. The main components of okara are protein (25.40-40.36%*)* and dietary fiber (14.5-55.4 g/100 g on dry basis) [4,5].

Nutritional properties of raw okara that was obtained as a byproduct from six soybean varieties during hydrothermal cooking (HTC) of soymilk were assessed. The composition and residual activity (rTIA) of trypsin inhibitors (TIs), contents of lectin, proteins, fats and carbohydrates, and energy values (EV) were correlated with the respective physicochemical properties of soybean and okara. Kunitz (KTI) and Bowman-Birk (BBI) TIs both comprised to okara rTIA. TIs content was higher in okara (5.19-14.40%) than in soybean (3.10-12.17%) that additionally enriched okara by cysteine. Low urease index activity indicated that okara was heated adequately to inactivate antinutritional factors. The proximate composition of raw okara, advantageous rTIA and a very low EV (2.74-3.78 kJ/g) qualify this byproduct for potential application in food preparation as a functional ingredient in dietary products.

The study was financed by the Serbian Ministry of Education, Science and Technological Development (TR31022).

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F P39

Improvement of the nutraceutical quality of grape seed oils

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Grape seed oil has a wide range of application being used in cosmetics (as a popular skin treatment), in medicine for his exceptional therapeutic properties and in food. Grape seed oil has a high content of triglycerides, especially unsaturated fatty acids such as oleic and linoleic acids. The nutraceutical effects of grape seed oils have been confirmed by its composition in essential fatty acids such as linoleic and linolenic acids, total phenols and total volatile compounds content as well as its antioxidant capacity.

The aim of this study is compositional characterization of grape seeds oils fortified using cold extraction of components from grape seed, using spectroscopic methods (IR, GC-MS, RMN). The NMR and IR analysis was conducted directly on the grape seed oils, without any other sample preparation, while GC-MS method was conducted on fatty acid methyl esters (FAME). The results show an improvement of grape seed oils quality.

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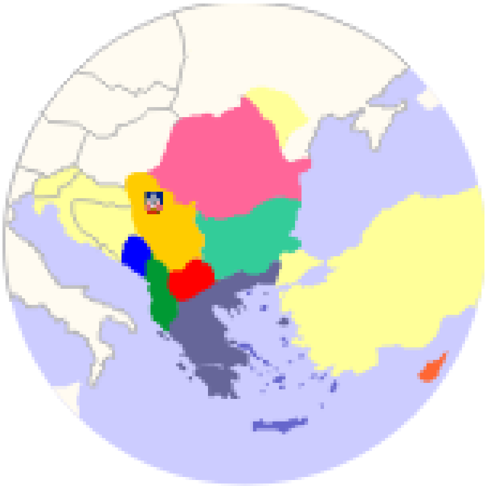
Career Day



Communicating chemistry - Bringing chemistry to the public

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Despite the fact that chemistry plays a pivotal role in our society and is the key-element for our scientific and technological progress, there is a strong reserved feeling from the wider society towards everything which is related with chemistry. Our beloved science has a very negative connotation which has a detrimental effect on the popularity of chemistry. Therefore, researchers and scientists should create an advanced dialogue with the wider society, tailored on the level of the specific public.

This lecture will illustrate the problems and challenges which chemists have to face whenever they communicate chemistry for a broad scientific-minded public and reveal several approaches to tackle them [1].

Furthermore, questions and practical problems will be answered.

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Designing scientific presentations: a toolbox for researchers

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Whether you are an experienced speaker or not, everybody knows the feeling, the last five minutes before your scientific lecture starts. A combination of excitement, doubts, fear and nervousness kicks in, which could have an unfavorable effect of your oral communication. Even more, during your presentation, as a speaker you have to entertain your audience for the whole lecture time, both vocally and visually.

This lecture will provide tools for speakers giving scientific presentations including tips and tricks on how to become a good or better speaker and to make your presentation more attractive and inspiring for the audience [1].

Furthermore, questions and practical problems from the audience will be answered.

References:

[1] a) M. Davis “Scientific Papers and Presentations” 2nd edition (2006), Elsevier; b) M. Carter “Designing science presentations: a visual guide for figures, papers, slides, posters and more” 1st edition (2013), Elsevier.

Publish, don't perish! The art of writing

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Writing a scientific paper is something that many scientists enjoy and others dread. The value of writing a paper in a concise, engaging and clear way, normally translates to a higher impact of your scientific work because top articles are normally well-written, read, remembered and highly cited, whilst poorly written papers are easily forgotten.

However, good writing is not simple and depends on many different factors as the journal, type of manuscript, concepts to report and readers, for example, showing that there is not a single, correct way to write a paper, because different approaches are possible [1].

In this communication, an overview of the elements of style and composition of a scientific paper will be discussed. In addition, different approaches for an effective and successful writing outcome will be reviewed and adapted to young chemists in the early stage of their career.

References

[1] a) M. Ashby *"The art of writing"* 6th Edition (2005), Cambridge; b) K. W. Plaxco, *Protein Science* **19** (2010) 2261; c) G. M. Whitesides *Adv. Mat.* **16** (2004) 1375.

Writing Proposals Efficiently and Effectively

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Writing of proposals is a difficult task which needs to be carried out by a chemist during his entire career. Proposals and projects are needed for getting financial support for many different activities like studying a Master, a PhD, carrying out a research project and establishing a research group, for example.

Thus, this lecture will be focused on the art of writing a grant proposal. Usually, the process of planning and of presenting your research ideas or results to the right person takes time and persistence to succeed. Thus, techniques and advices for an efficient way of writing proposals will be presented and discussed.

Some topics like the idea development and identification of the most appropriate funding sources and the basic components of a proposal will be discussed and the participants will also learn the common mistakes and reasons why sometimes well written proposals finally fail [1].

Furthermore, a brief discussion about the budget preparation and review criteria as well as some tips for writing successful proposals will also be carried out.

Finally, questions and doubts from the Audience will be discussed.

References:

[1] M. Druelinger “Writing Excellent Proposals” *ACS National Meeting* (2011), Denver (Colorado), USA.