BOOK of ABSTRACTS

25th Congress of Chemists and Technologists of Macedonia

19-22 9 2018
OHRID, R MACEDONIA

CXTM

Сојуз на хемичарите и технолозите на Македонија

Society of Chemists and Technologists of Macedonia

25th Congress of SCTM
with international participation

BOOK of ABSTRACTS

19–22 September 2018
Metropol Lake Resort
Ohrid, R. Macedonia

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Society of Chemists and Technologists of Macedonia
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The 25th Congress of SCTM is a EuChemS European Chemical Society **recognized event.**

Dear Colleagues,

Welcome to the 25th Congress of the Society of Chemists and Technologists of Macedonia. Although this is our silver jubilee, our society is celebrating more than 50 years of scientific meetings. The first conference, one of the first activities of our society, was organized in the 1960-ties and was a meeting between the faculties of the Institute of Chemistry at Faculty of Sciences and Mathematics and the Faculty of Technologists, both at the Ss. Cyril and Methodius University in Skopje. They gradually grew into biennial meetings and attracted participants outside of Macedonia. Beginning from the 18th Congress in 2004 all our meetings are held in the exceptional setting of Lake Ohrid. In 1994 our society started to organize students' scientific meetings and now the two alternate, so there is a congress organized by our society every year.

Since 2012 we have been using the Open Journal System to manage the editorial process of the *Macedonian Journal of Chemistry and Chemical Engineering* published by our society. In order to streamline the technical management of this congress and future such meetings, we have undertaken for the first time to implement the Open Conference System. You are all now familiar with the whole process of registering, submitting the abstracts etc. – at times you/we did encounter problems but overall we are satisfied with this platform and plan to use it in the future. For all of you who have smart phones, you will find the abstracts and schedule online which can be searched by various criteria. Furthermore, in line with the digital age we live in, for the first time we will not have a printed Book of Abstracts but only an electronic one. A draft version with all submitted abstracts along with the conference program was uploaded to the platform three weeks ago. The final version will be available after the conference and only the presented contributions will be included. Another first at this conference will be a Skype presentation on Saturday. We hope in the future to further improve the technical capabilities by streaming at least some of the lectures online.

Next year the world will be celebrating 150 years of Mendeleev's Periodic table of the chemical elements. Our society was involved from the very beginning two years ago – we immediately contacted our representative to UNESCO to give our full support for this important event marking one of the few discoveries in science that has withstood such a long test of time. It is nice to see the world united in a scientific achievement despite the extreme polarization in other areas. I believe you share my opinion that we are so fortunate to have chosen to pursue chemistry, the ever evolving science. Whenever I hear divisive undignified debates that take place so often now, the words of Sir Humphrey Davy in his discourse delivered at the Royal Society, in November 1825 echo in my ears: *Fortunately science, like that nature to which it belongs, is neither limited by time nor by space. It belongs to the world, and is of no country and of no age. The more we know, the more we feel our ignorance; the more we feel how much remains unknown; and in philosophy, the sentiment of the Macedonian hero can never apply, – there are always new worlds to conquer.*

From the more than 250 contributions given in this book we have a truly diverse body of researchers in many fields of chemistry. But more important than the number is the quality of the scientists presenting their new results: we have two exceptional keynote speakers, 10 invited speakers, 49 oral presentations and 195 poster presentations. Due to the traditional environment of tolerance in Macedonia, it is a truly unique regional conference bringing together the scientists from a very wide area.

I would like to thank sincerely the presidents of the Organizing and Scientific Committees, Prof. Viktor Stefov and Prof. Trajče Stafilov. Also, I must mention Assistant Prof. Jasmina Petreska-Stanoeva and Prof. Marina Stefova. I think this is the best team we could put together to make a really flawless organization. Furthermore, I would like to thank the Ministry of Education and Science of Macedonia, the Ss. Cyril and Methodius University in Skopje and the Goce Delčev University in Štip for their financial support, as well as the commercial sponsors that are given at the end of this book for their financial support and/or support in their products.

I do hope you will enjoy the scientific program of this congress, the interactions with colleagues from other institutions and countries and will build new relationships and collaborations. Most of all I would like to ask you to spend some time with the young researchers and students present here – for one of our main goals is also to build on the nexus between education and research and inspire and energize the young in the intricacies of the science of chemistry. I know I do not need to tell you to enjoy this magnificent lake, for us the most beautiful lake in the world, the inspirational crammed with extraordinary churches city of Ohrid and its unique heritage to world civilization.

Prof. Zoran Zdravkovski, president
Society of Chemists and Technologists of Macedonia

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KEYNOTE LECTURES (KL)

KL 1

ELECTROCHEMICAL NANO-IMPACTS: NEW INSIGHTS INTO NANOPARTICLES

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First the analytical need for nanoparticle detection will be introduced and electrochemical studies on suspensions of nanoparticles shown to allow the detection and characterisation of diverse nanoparticles at the single entity level. For electroactive nanoparticles such as those of silver, Ag, or iron oxide, Fe_3O_4, quantification of the charge associated with single collisional impacts, allows the sizing of the particles in the range from ca 100 nm down to less than 5 nm. The frequency of impact events permits particle concentrations to be estimated and the potential dependence indicates the chemical nature of the impact particles.

In many cases the electrochemistry reveals agglomeration or aggregation of the particles and since the monomers and agglomerated diffuse at different speeds the kinetics of de-agglomeration can be inferred in cases such as that of uncapped Bi_2O_3 particles where the electrochemical signals are dominated by the monomer signal whilst independent evidence shows significant agglomeration in bulk solution. Models for the extent of agglomeration have been developed.

Second the extension to the study, at the single entity, will be described in terms of the detection of bacteria, red blood cells, the doping of particles of solids and polymers and in nano-droplets will be reported.

Finally the possible nano-toxicity of silver will be discussed.

Keywords: nanoparticles, electrochemistry.

KL 2

HIGH PRESSURE RESEARCH OF ORGANIC AND COORDINATION COMPOUNDS. RETROSPECT AND PROSPECTS

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Crystals of organic and coordination compounds were actively studied by spectroscopic techniques already in the middle of the 20 century. The effect of high pressure on the reaction kinetics was used as a key to understand the mechanisms of chemical reactions in solution at ambient conditions. Since the late 1990s crystalline coordination and organic compounds are being actively studied at high pressures also by diffraction techniques. The pressures not exceeding 10 GPa are sufficient, to induce many interesting processes in these systems, including, among other, anisotropic strain, changes in molecular conformations, distortion or switching over of hydrogen bonds, proton migration, charge transfer, structural polymorphic transformations, recrystallization, solvation (more generally - formation of host-guest compounds), or, contrary, pressure-induced dehydration of crystal hydrates.

The phases formed under given temperature-pressure conditions are not necessarily the thermodynamically stable ones. Quite often the phases formed are metastable, but can be preserved during indefinitely long time. Moreover, quite often the thermodynamically stable phases cannot be formed, unless a special experimental protocol is used and a recrystallization from a fluid phase is possible. The phenomenon is termed “kinetic control” and is related to the large difference in the rates of nucleation and nuclei growth of different phases, not directly proportional to their relative stabilities. The protocol of compression and decompression, the choice of pressure-transmitting fluid or/and of the starting polymorph, the sample size, temperature, irradiation by light, the presence of other phases in the same cell, and other factors can be critically important for the formation of selected phases, their recrystallization or solid-state transformations on hydrostatic compression.

High-pressure research today is an extensive research field. The main focus now is on understanding new phenomena occurring at high pressure. Still, it is possibly time to look backwards to the early years of the high pressure research, when pressure was used as a tool, in order to understand the properties and the transformations of compounds that occur under ambient conditions. Examples of recent research, when high pressure experiments helped to understand crystallization, phase transitions and solid state chemical reactions also at ambient conditions, are discussed in relation to the concepts of reaction cavity, chemical pressure, feed-back phenomenon and mechanically responsive crystals undergoing thermo- or photo-transformations.

Keywords: reactivity of solids, polymorphism, phase transitions, hydrogen bonds, photocrystallography.

KL 3

MULTISCALE MODELLING OF METAL OXIDE-SURFACES – AND THEIR AQUEOUS INTERFACES

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Not presented.

INVITED LECTURES (IL)

IL 1

NANOPARTICLE CATALYSIS: NANOMORPHOLOGY AND INTERFACIAL STRUCTURE

Christopher Batchelor-McAuley

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When operated in real world devices, present state-of-the-art electrocatalysts do not appear to perform as well as predicted on the basis of measurements made in laboratories using model liquid half cells (see for example Stephens *et al.* Science 2016, 1378). The origins of this discrepancy in behaviour may be numerous but one possible explanation lies in the different current densities at which the catalyst is operated at in real devices as compared to idealised laboratory conditions. At high current densities a fundamental bottleneck in the redox reaction may exist. Consequently, there is presently a drive towards the development of methodologies by which nano-electrocatalysts can be controllably studied at high-current densities. The purpose of this research is to enable the catalyst to be studied under conditions that - in some ways - more closely mirrors those found in real world applications; hence, allowing the operative chemistry to be illuminated. The study of catalytic reactions at the single particle scale is one route by which this might be achieved.

This lecture aims to give an overview of our current progress in the study of electrochemical catalytic reactions at the *individual* nanoparticle scale. By using the proton/hydrogen redox couple as an archetypal ‘inner-sphere’ redox process we explore how single particle activity and electroactive surface area measurements can be simultaneously made and further explore what information can be attained regarding the nanomorphology of the catalytic entity. It is shown how at the single particle scale the hydrogen oxidation reaction becomes limited not by the mass-transport of the dissolved gas but by the rate of adsorption of hydrogen to the platinum surface.

References:

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[2] X. Li, C. Batchelor-McAuley, S.A.I. Whitby, K. Tschulik, L. Shao, R.G. Compton *Angew. Chem. Int. Ed.* 2016, 55, 4296-4299.

Keywords: hydrogen, mesoporous nanoparticles, electrocatalysis.

IL 2

STRONG HYDROGEN BONDS – STRUCTURES, PROPERTIES, EFFECTS

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Although weak compared to electrostatic and covalent bonds, hydrogen bonds D-H···A_n (D = donor atom, A = acceptor atom, n = number of acceptor atoms) are of major importance in life and economy as well.

So called weak hydrogen bonds, i.e. those with bond energies $\Delta E \leq 10$ kJ mol^{-1}, play an essential role in biological processes like DNA structure building and replication or in nervous conduction. Against that, strong hydrogen bonds, i.e. those with bond energies $\Delta E \geq 60$ kJ mol^{-1} are commonly combined with ferroic properties and phase transitions and high protonic conductivity of the respective compounds.

In this context, the peculiarities of the crystal, molecular, and bonding structures and of the hydrogen bond induced phase transitions of solid acids and acid oxo salts and organic molecular complexes analyzed systematically by means of DSC, DTA, TG/DTG, powder and single crystal X-ray and neutron diffraction and vibrational spectroscopy are presented and discussed.

Keywords: hydrogen bond; XRD; spectroscopy.

IL 3

DESIGN OF PHOSPHATE INTERCALATION COMPOUNDS: SYNTHESIS APPROACHES, STRUCTURE AND MORPHOLOGY CONTROL

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Electrochemical energy storage systems play a significant role in renewable energy strategy and their importance will grow steadily as a solution to meet future energy needs and overcome some environmental problems of our planet. Among the different types of batteries, lithium-ion batteries (LIBs) are recognized as the most effective technology for energy storage with a variety of applications due to their outstanding energy and power capability. More recently, sodium-ion batteries (SIBs) have attracted considerable interest for large scale energy storage due to the practically infinite sodium resources and their low cost.

The operation of a rechargeable LIB and SIB is based on intercalation reactions (Li^+ and Na^+) that take place on both cathode and anode of the electrochemical cell though a reduction/oxidation mechanism. There are three main classes of inorganic intercalation compounds that show exceptionally attractive properties as cathode materials in LIBs: (i) Layered transition metal oxides with main commercial representatives $LiCoO_2$ and $LiCo_{1-x}M_xO_2$ (M being mixture of Ni, Mn and Al); (ii) Spinel-type transition metal oxides based on $LiMn_2O_4$; (iii) Polyanion compounds containing different XO_4^{y-} units (X = S, P, Si, B, Mo, W) that comprise a variety of chemical compositions and structure diversity, of which the industrial use of $LiFePO_4$ has been demonstrated.

The present contribution is devoted to both lithium and sodium olivine-type phosphate intercalation compounds having compositions $AMPO_4$ (A^+ = Li, Na; M^{2+} = Fe, Mn, Co, Ni). Phospho-olivine family exhibits promising application primarily in electric vehicles due to its excellent safety related to the stable three-dimensional phosphate framework, high capacity, good thermal and cycling stability, low cost (particularly for Fe and Mn members) and environmentally benign. Because of the very low electronic/ionic conductivity and anisotropic Li^+/Na^+ mobility, the electrochemical properties of the phospho-olivines are extremely sensitive to the preparation routes that affect the microscopic and macroscopic characteristics of the materials. In this regard the choice of an appropriate synthesis route is the key to realizing the desired properties.

The research here presented is focused on several aspects: (i) Our achievements in the development of new synthesis methods mainly based on “soft chemistry” rules that are applicable for the preparation of all members of the phospho-olivine family as well as solid solutions between them; (ii) Combination of diffraction (XRD, Rietveld analysis, SAED), spectroscopic (IR and Raman spectroscopy) and microscopic (SEM, TEM, HRTEM) methods to examine in details the crystal structure and morphology characteristics (shape and size of particles, particle size distribution, agglomeration); (iii) Understanding the relationship between synthesis method, structure, morphology and electrochemical properties which plays a crucial role in the design of effective olivine-type electrode materials in lithium-ion and sodium-ion batteries.

Acknowledgment: The author is grateful to the financial support from the National Science Fund of Bulgaria (Project DN09/13).

Keywords: Olivine-type electrode materials, intercalation, lithium-ion batteries, sodium-ion batteries, nanostructured materials.

IL 4

NOVEL NANOCARRIERS: DNA ORIGAMI BASED NANOSTRUCTURES AND BORON NITRIDE NANOTUBES

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There is an increasing effort to utilize nanomaterials and nanostructures for drug targeting and delivery. However, a number of parameters in the design of nanocarriers including toxicity, stability, degradation/dissolution, size and stability/retention in the circulatory system should be considered. The recent paradigm is to construct or use nanostructures possessing most of these properties in developing effective drug carrier systems. In this context, DNA offers a unique opportunity since Watson-Crick based paring can be utilized to generate variety of novel structures. In addition, a more recently recognized nanomaterial, boron nitride nanotubes (BNNTs), could be good candidates for such applications. In this talk, our effort to utilize DNA-origami based nanostructures, gold nanoparticles and BNNTs as drug and antisense oligonucleotide carriers are summarized.

Keywords: nanocarriers, DNA origami, boron nitride nanotubes, delivery, gene silencing.

IL 5

ANALYTICAL CHALLENGES IN THE IMPLEMENTATION OF THE MINAMATA CONVENTION

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Not presented.

IL 6

ENZYME IMMOBILIZATION TODAY

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The application of enzymes in modern biocatalysis is focused in various fields, such as biomedicine, biosensors or bioreactors for different industries or environmental protection. Therefore immobilization methods which are chosen fit in the desired application field. We may choose among different immobilization methods to prepare a biocatalyst for its application. Modern immobilization methds allow enzyme immobilization with or without a carrier in the form of micro- or nano-particles.

A very simple method for enzyme immobilization without a carrier is the production of the so called cross-linked enzyme aggregates or CLEAs. This is also a very cheap method where there is no need for enzyme purification prior the CLEAs formation because the enzyme purification and immobilization sre joined in one step. CLEAs are suitable for the use in biosensors and in bioreactors due to the very high enzyme activity and stability in this form which as a consequence enables lower energy demand in such a process.

Magnetic nanoparticles (MNPs) of different core materials are a typical example of carriers for enzyme immobilization today. Advantages and applicability of MNPs has opened up a large scope of possibilities in industrial and environmental biocatalysis, as well as in biomedical technology. Comparing to larger sized particles, the main advantage of MNPs is in their high surface-to-volume ratio, which contributes to a higher surface energy and to excellent magnetic properties. MNPs are typically crystals of inorganic elements for which the largest characteristic dimension is approx. 1-100 nm. Their inorganic magnetic core is usually surrounded by layers of functional coatings, which are designed according to the application of the final product. .

Different enzymes have been immobilized in the form of previously described CLEAs and on MNPs with different coatings. The final activity of the so immobilized enzymes depends on the immobilization method and on all substances that are used in the immobilization procedure. In many cases hiperactivation of the enzyme may be reached.

Acknowledgements: Slovenian research agency.

Keywords: enzymes, immobilization, cross linked enzyme aggregates, magnetic nanoparticles.

IL 7

FUNCTIONAL AND SMART NANOFIBERS FOR ADVANCED AND BIOMEDICAL APPLICATIONS

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Continuous nanofibers produced by electrospinning possess extraordinary features, including high surface area to volume ratios and high porosities. The versatility of the technology allows to obtain fibres from a wide range of polymers and blends, fibers loaded with drugs and particles, and organic-inorganic hybrids. Therefore, multi-components and multi-functional nonwovens with controlled fiber dimension, orientation and functionalization ca be produced, possessing unique properties that make them attractive for a wide range of applications, including techno-textile, membranes for air and water treatment, biomedical applications, electronic devices, catalysis, etc.

This talk will present some selected applications and frontier research activities on nanofibers produced by electrospinning, highlighting the possibility to smartly control and modulate material properties thanks to proper combinations of both commercial and newly synthetized polymers, surface functionalization techniques and different instrumental setups. The talk will focused in particular on the use of electrospun materials in biomedical applications and as functional and smart materials for advanced applications. Artificial tendons and fiber-gel composites mimicking the extracellular matrix of biological tissues will be presented for uses in tissue engineering and drug delivery from electrospun fibers and encapsulated particles will be discussed. Surface functionalization strategies to produce affinity membranes for the isolation of target cells and other biological substances will be described. Smart electrospun responsive materials for advanced applications will be also presented, with a particular focus on shape-memory fibers and membranes, mechanochromic and stress-sensing materials and self-healing materials.

Keywords: electrospinning, nanofibers, tissue engineering, drug delivery, shape-memory, mechano response, self-healing.

IL 8

FILLER SURFACE-INDUCED EFFECTS IN POLYMER COMPOSITES: RELATIONSHIP WITH OVERALL COMPOSITE'S PROPERTIES

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Not presented.

IL 9

METHODOLOGICAL DEVELOPMENT OF ADVANCED VOLTAMMETRIC TECHNIQUES: THEORY AND APPLICATION

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The lecture concerns recent methodological advances of pulse voltammetric techniques, in particular square-wave voltammetry [1]. Experimental examples span over areas such as coupled electron-ion transfer processes, charge transfer across liquid|liquid interfaces, to electrocatalysis with noble metal nanoparticles. Particular emphasis will be given to new methodological concepts such as multisampling square-wave voltammetry [2], electrochemical faradaic spectroscopy [3], potential corrected square-wave voltammetry, cumulative voltammetry, and for the first time proposed, a hybrid technique between differential pulse and square-wave voltammetry. A series of electrode mechanisms are critically considered and compared in order to reveal the benefits and drawbacks of different square-wave voltammetry related voltammetric techniques.

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Keywords: electrochemistry, voltammetry, theory.

IL 10

SINGLE MOLECULE TEMPERATURE-DEPENDENT THEORETICAL SPECTROSCOPY WITH COMBINED ATOM CENTERED DENSITY MATRIX PROPAGATION AND TIME SERIES ANALYTIC METHODS

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Most of the current theoretical spectroscopic studies of molecular systems are based on diagonalization of mass-weighted Hessian matrices for minima on the studied potential energy surfaces. These data, although being extensively used for interpretation of experiments, actually rely on the “double harmonic” approximation and refer to 0 K. Many experimentally realizable situations, on the other hand, take place at temperatures rather high above the absolute zero. At the same time, the “normal” or “local” - mode vibrations of polyatomic species may seldom be approximated by the model of harmonic oscillator. A rather important question that thus arises is: “can one include *at the same time* both the effects of anharmonicity*and* finite temperature in *single-molecule theoretical spectroscopy* in a reliable and computationally-feasible manner”?

In my talk, I will present the ongoing efforts in our, as well as other research groups, towards the previously implied aim. Our own efforts are directed towards development and implementation of hybrid statistical physics – time series analytic methods in theoretical single-molecule vibrational spectroscopy.

The statistical physics phase in our methodology is based on *ab initio*, DFT or semiempirical molecular dynamics simulations, carried out with the atom-centered density matrix propagation scheme (ADMP). This particular method belongs to the extended Lagrangian approaches to molecular dynamics, based on propagation of the density matrix, using Gaussian-type basis functions. ADMP simulations are performed in the microcanonical (*NVE*) ensemble, initially injecting certain amount of nuclear kinetic energy to the system (which is further distributed among the atoms) in order to reach the finally desired temperature. To avoid any distortion of the system’s dynamics, no thermostats are applied to maintain constant temperature. MD results are further analyzed within the framework of the linear response formalism, utilizing various time-correlation functions (TCFs). Aside from the most widely used TCFs (velocity-velocity ACF and the dipole moment ACF), we also analyze certain partial ACFs, utilizing time series signal analysis techniques. To recover both the frequency content of the time-dependent signal and its time variation, aside from Fourier transformation (FT) techniques, we also implement the wavelet as well as the short-time FT approaches. With the last two techniques in particular, one can follow the time-dependent structural changes in conformationally flexible molecules.

The developed methods, their advantages and drawbacks are illustrated on several model systems: formic acid, 1-naphtol and $H_2@C_{60}$. The superiority and advantageous computational cost of signal-analysis techniques in the case of large systems is particularly demonstrated.

IL 11

MINERALS FROM MACEDONIA. SPECTRA-STRUCTURE CORRELATIONS BY COMBINED USE OF VIBRATIONAL (IR AND RAMAN) SPECTROSCOPY, X-ray DIFFRACTION AND THERMAL ANALYSIS

Petre Makreski

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In the last two decades, comprehensive studies regarding the collection, separation, identification and systematization of around 100 minerals which comprise about 70 % of the known diverse mineral-type wealth of Macedonia have been carried out [1]. The overall mineral research was focused on two aspects: i) elucidate vibrational spectral behavior complemented to structural features and ii) develop and optimize methods for selective separation and elimination of the matrix elements to accurately determinate minor and trace elements in minerals.

This work is aimed to outline some novel vibrational spectroscopy findings reinforced or reconfirmed by X-ray diffraction studies and thermal analysis undertaken solely on Macedonian minerals. Thus, despite the importance to describe the spectra-structural features, a particular accent will be stressed to selected examples revealing interesting and intriguing results encompassing: Raman spectra peculiar phenomena as a result of presence of rare-earth elements in some nesosilicates [2], light-induced [3,4] and mechanochemically-assisted [5] phase transition in sulfide minerals, discrimination of common tectosilicates [6] and very rare Tl-sulfides [7] solely relying on far-IR and Raman spectroscopy, respectively; presence of Fe^{3+} content in the monoclinic epidotes with variable (Fe^{3+},Al) composition by monitoring the IR spectra [8], possible (Fe,Mg) cation combinations in the Y structural sites of tourmalines [9], thermally-induced studies of very complex hydrogen arsenates to support band assignments [10], etc.

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Keywords: vibrational spectroscopy, minerals, X-ray diffraction, thermal methods.

IL 12

CRYSTAL STRUCTURE SOLUTIONS FROM POWDER DIFFRACTION DATA

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Research in solid-state chemistry, physics and structural biology, heavily relays on knowing the precise atomic or molecular structure of the studied material. Crystalline materials feature well-ordered structures, with long-order periodicity of the building blocks, as guided by symmetry. The infinitely repeating units collectively produce characteristic diffraction patterns when X-rays, electrons or neutrons are being scattered from the material. The diffraction signature can be collected and analyzed, revealing the relative spatial distribution of atoms in the unit cell, allowing for a solution of the crystal structure.

Arguably, the best method for solving crystal structures is single crystal diffraction, for which relatively large and high-quality single crystals are necessary. However, many important materials do not readily crystallize as single crystals. Myriad crystallization strategies, including countless recrystallization attempts, are oftentimes employed to grow crystal of suitable size. These efforts do not warrant success — a legion of important materials can be only obtained as a polycrystalline bulk or powder, no matter the efforts. In cases as such, the remaining alternative for solving the crystal structure is powder diffraction. Crystal structure solution from powder diffraction data, more often than not, is a very tedious and challenging process. Diffraction data is being collected from carefully ground powder (to mitigate the effect of preferred orientation of particles). The data is integrated in form of a one-dimensional diffraction pattern, featuring characteristic Bragg intensities. The position of the Bragg peaks (measured in 2Θ values relative to the wavelength of the X-rays, neutrons or electrons) is used for indexing of the unit cell and obtaining the cell parameters and possible symmetry. This information is used to initiate the structure solution process, which can be performed either in direct or reciprocal space. Finally, the solved crystal structure is being refined using the Rietveld method.

In this talk, we will discuss the recent advancements in *ab initio* structure solutions from powder diffraction data, measured using X-ray and neutrons. We will present various examples of solved and refined crystal structures of cements, pharmaceuticals, organic materials, inorganic materials, hybrids and metal-organic frameworks. Moreover, we will discuss several advances of powder diffraction over single crystal diffraction, especially in the fields of *in situ* structural studies and monitoring chemical reactions and physical processes (photo-activations, thermal-activations, gas-dosing, and milling), and performing qualitative and quantitative analyses.

Keywords: crystal structure solution, diffraction, powder.

IL 13

DEVELOPING NANO-ENBALED WATER TREATMENT TECHNOLOGIES: CHALLENGES AND BARRIERS

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Not presented.

Inorganic Chemistry and Technology, Inorganic Materials and Metallurgy (ICTM)

ICTM O-1

RECYCLING OF VALUABLE METALS FROM SPENT LITHIUM-ION BATTERIES

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A commercial lithium ion battery (LIB) consists of a cathode, an anode, a separator, and electrolyte. The cathode assembly mainly consists of Al foils (collector), active cathode materials, carbon black, and a binder polyvinylidene fluoride (PVDF), and the anode mainly consists of Cu foils (collector), graphite and a binder PVDF. Currently, both pyrometallurgical and hydrometallurgical methods have been used in the recycling of spent lithium ion batteries. Compared to the pyrometallurgical, hydrometallurgical methods are more widely used as it is more environmentally friendly, and can achieve a higher efficiency of metal recovery.

The ideal process of recycling, should characterized by maximum amount of recovered metals by minimum number of steps as well as minimum amount of used reagents. One of major problems in LIB recycling is dissolution process of the binder PVDF from the cathode materials by organic solvent which is difficult and expensive. As applied to the spent LIB, the process must facilitate the complete separation of the powdered active materials from the current collector metal foils and the binder, before leaching process. An obvious candidate that satisfies the above objectives can be a thermal treatment of the waste cathode assembly at an elevated temperature.

In this paper, a process including a thermal treatment and leaching is developed to recover transition metals from spent LIB. The obtained results confirms that thermal treatment helps improves the leaching efficiency of all valuable transition metals, defined as the percentage of the metal leached out from the active electrode materials.

Keywords: lithium ion battery, transition metals, recycling.

ICTM O-2

RECYCLING OF Nd-Fe-B MAGNETS BY HYDROGEN DECREPITATION

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Rare earth magnets based upon neodymium-iron-boron (NdFeB) are employed in many clean energy and high tech applications, including hard disk drives (HDDs), motors in electric vehicles and electric generators in wind turbines. When compared to other permanent magnets, such as Alnico and Ferrite, NdFeB magnets offer substantially stronger magnetic fields per volume, which make them suitable for high performance products with compact designs.

The key elements in manufacturing NdFeB magnets are rare earth elements (REEs) such as neodymium and dysprosium. These elements have been subject to significant supply shortfalls in the recent past. REE and NdFeB magnet production is dominated by China and the risk of this monopoly has been widely recognized. These all serve to limit the global availability of neodymium [1,2].

Recycling of NdFeB magnets contained within redundant electrical equipment could provide a secure and alternative supply of these materials. Various recycling approaches for the recovery of sintered NdFeB magnets have been explored by industry and academia. These include direct reuse, waste-to-REE, waste-to-alloy, and magnet-to-magnet approaches. Except direct reuse, these processes may use hydrometallurgical or/and pyrometallurgical methods. The advantages and disadvantages of these methods are discussed elsewhere [3,4].

It has been reported [5,6] that hydrogen can be used as an effective method of recycling NdFeB by utilising the hydrogen decrepitation (HD) process to turn solid sintered magnet into a demagnetised powder for further processing.

In this work, sintered Nd-Fe-B magnets, dismantled from HDDs, were processed without prior removal of the Ni protective layer using the hydrogen processing (hydrogenium decrepitation - HD) as an alternative recycling method.

The gas sorption analyser have been used to determine the quantity of the hydrogen absorbed by a sample of magnet, under controlled pressure (1, 2, 3 and 4 bar) and temperature (room, 100, 300 and 400 ^{0}C) conditions, using Sieverts' volumetric method. The composition and morphology of the starting and the extracted/disintegrated materials was obtained via ICP, XRD and SEM analyzes.

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Keywords: NdFeB magnet, recycling, hydrogen decrepitation.

ICTM O-3

EXTERNAL MAGNETIC FIELD-INDUCED AGGREGATION AND SEDIMENTATION PROCESSES ARISING IN MAGNETIC FLUIDS

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The spectral analysis of external magnetic field influence on hydrothermally synthesized $CoFe_2O_4$, $FeFe_2O_4$, and $MgFe_2O_4$ nanoparticles in ferrofluid was presented. In order to control particle growth, stabilize particles against aggregation and enhance dispersibility in an aqueous medium, surface coating was achieved using citric and oleic acid, popular surfactants in preparation of magnetic particles for medical applications. New experimental settings were developed for the study of behavior of ferrofluids with the applied magnetic field strength in the range of 30-400 mT. Field-induced change of transmittance occurred and a precipitation of all studied samples was obtained. Contrary to the linear aggregates of colloidal $CoFe_2O_4$ and $FeFe_2O_4$, approximately spherical aggregates were observed in the case of $MgFe_2O_4$. The behavior of this kind of ferrites is in accordance with its soft magnetic nature. In all cases, the surface modification resulted in decreased dipole-dipole interactions between magnetic cores, and consequentially less precipitates were noticed. All citrate coated nanoparticles have shown stronger magnetic response in comparison to the oleate modified samples. The aggregation of nanoparticles potentially increases cytotoxicity although it is still unknown how aggregates formed in external magnetic field affect biological responses when ferrites are used in biomedical applications. Regarding non-linear clustering of $MgFe_2O_4$ suspensions, it can be concluded that its excretion from the organism could be likely easier and faster when used in diagnosis and/or therapy. Therefore, more attention should be paid to the low toxic $MgFe_2O_4$ for its medical application.

Keywords: ferrofluid aggregation, external magnetic field, light transmitting measurements.

ICTM O-4

STUDY OF PROTON CONDUCTIVITY ON POWDER SAMPLES USING XRD

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The study of proton conductivity is important in many different fields and disciplines. This property can be used in sensors, electrodes to determine glucose or cholesterol, in chemical reactors for hydrogenation and dehydrogenation industries and as materials for so called “Proton Exchanging Membranes” (PEM) in hydrogen fuel cells or “Solid Oxide Fuel Cells” (SOFC). The large family of proton conductors includes also salts of oxoacids, which have been studied in our department for several years. Proton conductivity was observed in crystals of hydrogen phosphates, sulfates, selenates or dihydrogen phosphates, where the cation was a nitrogen-containing organic base. The conductivities, whilst not high, were still several orders of magnitude higher than for insulators. We have prepared and described these new compounds, studied their structural properties by single crystal X-ray and neutron diffraction in combination with molecular spectroscopy and measured proton conductivity on oriented crystals. We were able to define the direction of conductivity in these crystals.

The conductivity mechanism in this type of crystals is not definitely clear. Proton transfer could occur via either the vehicle mechanism or the Grotthus mechanism. In anhydrous salts, the lack of water molecules excludes application of vehicle mechanism. But the application of Grotthus mechanism should cause disorders of the ions through which the protons are transferred at the conditions of proton conductivity. The best way how to study this phenomenon should be single crystal structure determination under the conditions of proton conductivity. But the realization of such experiment is not technically simple task.

For the first information, about existence of proton conductivity in any compound, we have tried to study this property by measurement on powder samples. The results are given in this presentation. Among our (mostly first prepared) samples we have also studied well known proton conductor $CsHSO_4$. This sample exhibit proton conductivity in powder form, and the value is comparable with measurement on single crystal. We have adapted our sample holder in PANalytical X´Pert Pro MPD diffractometer to be possible to keep the sample under high voltage (DC) during measurement. And we have studied its diffraction pattern without and under the conditions of proton conductivity. On approx. 60 % diffraction lines we have observed broadening and in some cases also the significant shift of diffraction lines both to higher and smaller angles. The analysis of this modified pattern can show, which diffraction lines are affected by proton transfer and define the “direction” of conductivity in the crystal, even the measurement is made on powder sample.

Keywords: proton conductivity, powder samples, in situ XRD measurement.

ICTM O-5

PREPARATION AND MICROSTRUCTURAL ANALYSES OF NANOLAMINAR CERAMIC MATERIALS

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Materials belonging to the Mn+1AXn (where M is an early transition metal, A is a group III or IV element and X either C or N) group have interesting nanolaminar structure which promise various technical applications. One of them are materials with high radiation resistance.

We prepared a series of materials belonging to MAX group. Especially Ti_2AlC have excellent mechanical properties and high temperature and oxidation resistance. Ti_2SnC has interesting micromechanical properties. All materials were characterized by classical methods and in several cases were also studied their microstructural properties.

Acknowledgements: Czech Science Foundation No. 18-21677S.

Keywords: MAX, carbide, nanolaminar.

ICTM O-6

TRIAZINES AS STARTING MOLECULES FOR NOVEL NONLINEAR OPTICAL MATERIALS

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Nonlinear optical (NLO) effects arise from nonlinear polarisation of a dielectric medium in oscillating electric field, usually achieved by pulse lasers. Such effects find a wide range of applications, for example in laser frequency conversion, optical communication and data processing. Nitrogen containing heterocycles are known to be promising building blocks for NLO materials, mainly because of their high polarisibility and a lack of color. Moreover, triazines in particular undergo interesting addition reactions leading to chiral products, which further increase the chance of a favorable crystal structure.

The potential NLO properties were predicted by DFT calculations for both the starting molecules and their reaction products and a range of crystalline samples was prepared. New materials were characterised by vibrational spectroscopy and X-ray diffraction. Finally, for materials of the right symmetry, second harmonic generation efficiency was measured on powder samples.

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Keywords: nonlinear optics; second harmonic generation; vibrational spectroscopy.

ICTM O-7

CO-PROCESSING OF ALTERNATIVE FUELS IN CEMENT INDUSTRU – QUALITY, PROCESS AND ENVIRONMENTAL ASPECTS

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Modern lifestyles and technological development contribute to increasing the generation of waste. On the other hand, production of cement consumes both large quantities of raw materials and fuel, and produces substantial CO2 emissions. Cement kilns have a number of characteristics which make them ideal installations in which alternative fuels can be valorised and burnt with no impact to the environment. These alternative materials can be either waste or by-products from other processes.

This paper will present quality aspects of selection and usage of alternative fuels in cement kilns, as well as benefits and potential impact to society and environment.

Alternative fuels must have the appropriate characteristics obtained by proper selection in order to avoid malfunctions of the kiln and avoid potential impact to environment. Therefore, intermediary stages for the preparation of wastes are needed in order to ensure required quality of the alternative fuels.

Some materials which the cement industry has utilised as alternative fuels have both useful mineral content and recoverable calorific value. Therefore, the distinction between alternative fuels and raw materials is not always clear.

The use of alternative fuels is a well proven and well-established technology in most of the European cement industry and this has been the case for more than 40 years. According to the data from Cembuerau, in 2017 about 41 % of the thermal energy consumption in the European cement industry originated from alternative fuels.

The use of waste as alternative fuels is technically sound as the organic part is destroyed and the inorganic part, including heavy metals, is trapped and combined into the product.

Usage of alternative fuels and raw materials in cement plants is an important element of a sound waste management policy. Through this valorisation the cement industry also contributes to reduction of emission of green-house gasses. This practice not only promotes waste energy recovery and recycling while creating opportunities for new jobs, but also saves non-renewable resources.

Keywords: Cement industry, co-processing of alternative fuels, alternative raw materials, GHG.

ICTM P-1

EFFECT OF HIGH-TEMPERATURE HEAT TREATMENT ON STRUCTURAL PROPERTIES OF METAKAOLIN-BASED GEOPOLYMER SAMPLES

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Considering geopolymers as inorganic polymers, they are actually amorphous network of interlinked silicate and aluminate groups, so they could be prospective ceramic precursors for materials with defined dimensions obtained by casting and firing, but not from powder processing. Since the geopolymer producing requires the silicon and aluminum bearing materials there are a variety of the initial starting materials. In this research, the starting material is metakaolin, which was obtained by calcining domestic kaolinite clay from Rudovci, Lazarevac, Serbia. Initally, the aqueous solution of NaOH and sodium silicate are prepared as activators of used material. The condensation and polymerisation reactions occurred at room temperature. The prepared geopolymer slurries were cast into the designated near shape and allowed to cure for 28 days prior to sintering. After the curing, obtained geopolymers were treated at high temperature 600 °C up to 1000 °C in controled conditions to follow phase transformation and dimensional stability as well as mechanical properties of processed samples. All samples were characterized by XRD, FTIR and SEM analysis, providing complementary and valuable information on the investigated materials. Annealing of geopolymer samples at 900 °C and 1000ºC led to a considerable reduction of oxygen and formation of the complex porous structure. Additionally, new semi-crystalline and crystalline phases appeared. In conclusion, this route of ceramics production has advantages associated with improving dimensional stability instead of conventional ceramics processing including the powder pressing and sintering.

Keywords: inorganic polymer, metakaolin, geopolymerization.

ICTM P-2

RADIOLOGICAL AND PHYSICOCHEMICAL CHARACTERIZATION OF GEOPLYMER

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This paper outlines to produce an environmental friendly, energy saving, clean technology to conserve the natural environment and resources using a metakaolin as a precursor for synthesis of inorganic polymer (geopolymer). The aim of this study was determination of physical-chemical, as well as radiological characteristics of kaolin and products of alkali-activated thermaly treated kaolin (geopolymer). Also, the aim of presented research was to investigate the possibility of application of kaolin as raw materials for obtaining geopolymer materials as a relatively new materials in a building material industry. Activity concentration of ^{40}K and radionuclides from the ^{238}U and ^{232}Th decay series in kaolin, metakaolin and geopolymer were determined as well as the absorbed dose rate rate (D) and the annual effective dose rate (E), calculated in accordance with the UNSCEAR 2000 report, are also presented in this paper. Measured natural activity concentrations in the alkali-activated material (geopolymer) were the lowest. Physicochemical characterization of all samples was conducted using X-ray diffraction (XRD), Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), zeta potential, BET method and X-ray photoelectron spectroscopy (XPS). Thus, polymerization of kaolin to inorganic polymer was completely monitored.

Acknowledgements: Ministry of Education, Science and Technological Development of Republic of Serbia, Project numbers: [III 45012].

Keywords: inorganic materials, geopolymer.

ICTM P-3

UNEXPECTED FORMATION OF *cis*-[$(DMSO)_2ClCu^{II}(\mu\text{-}Cl)_2Cu^{II}Cl(DMSO)_2$] IN THE REACTION OF *trans*-[$CuCl_2(DMSO)_2$] WITH THE THIOHYDANTOIN TYPE LIGAND

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In the reaction of well-known *trans*-[$CuCl_2(DMSO)_2$] complex with the polydentate thiohydantoin type ligand, 3-[(2-hydroxybenzylidene)amino]-2-thioxoimidazolidin-4-one [1], unexpected *cis*-[$(DMSO)_2ClCu^{II}(\mu\text{-}Cl)_2Cu^{II}Cl(DMSO)_2$] complex was formed predominantly as the final stable product, which structure was confirmed by single crystal X-ray crystallography (Fig. 1). Till now, only one procedure was reported, based on a specific preparation via decomposition of a tetranuclear [$Cu_4Cl_8(DMSO)_8(hmta)$] complex [2].

Starting ligand of thiohydantoin type is mostly recovered, while the minor amount is coordinated to Cu(II) ion. Coordination of the ligand is confirmed by different spectroscopic methods [3], but for the final elucidation of the structure of this minor product and the coordination mode the X-ray analysis is needed.

As the *cis*-isomer could not be obtained by direct synthesis and in our case is not obtained by decomposition of another complex, our investigation is directed to resolving the mechanism of this reaction and the role of the presence of the starting ligand in the isomerization of *trans*-complex to *cis*-form by either experimental or theoretical methods.

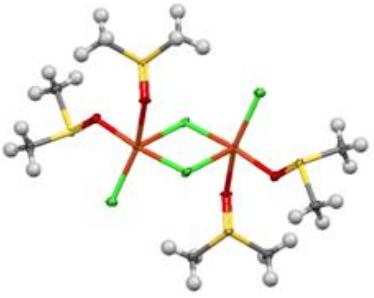

Figure 1. *cis*-[$(DMSO)_2ClCu^{II}(\mu\text{-}Cl)_2Cu^{II}Cl(DMSO)_2$] complex

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Keywords: Cu(II) complexes, thiohydantoins, cis-isomer.

ICTM P-4

MICROSTRUCTURE ANALYSIS AND ADSORPTION PROPERTIES OF METAKAOLIN BASED GEOPOLYMER SAMPLES

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There is potential use of alumosilicate natural or waste materials for synthesis of inorganic polymer materials through a geopolymerization as an alternative in removal process of metal ions Cd^{2+}. Metakaolin as alumosilicate solid raw material is the dehydroxylation product at 750 °C of the mineral kaolin of domestic origin. The influence of alkali activation, i.e. different concentration of NaOH (2M, 4M, 6M and 8M) as a component of alkali activator mixture on the process of geopolymerization of metakaolin was investigated. Also, process of aging time of geopolymer samples is followed by some analytical methods: X-ray Powder Diffraction, Fourier Transform Infrared Spectroscopy. The microstructure of metakaolin and metakaolin based geopolymer samples were analyzed by Scanning Electron Microscopy. The samples show a porous microstructure formed by unreacted micron size particles and a geopolymeric matrix that is formed during the geopolymerization process. Also zeta potential of all samples was measured. It was observed that the zeta potentials of geopolymer less positive than that of alumina particles and less negative than that of silica particles at all pH analyzed. Furthermore, based on the analysis of adsorption efficiency, microstructure and mineral structure, the difference between geopolymer and metakaolin on the performance of immobilizing cadmium ions have been discussed. The kinetics of adsorption can be represented by pseudo-second order equation. The results of cadmium ions adsorption experiments were best fitted by Freundlich adsorption isotherm for all investigated adsorbents.

Keywords: inorganic polymer, geopolymerization, cadmium, adsorption, zeta potential.

ICTM P-5

SURFACE MODIFICATION OF GOLD BY HETEROCYCLIC COVALENTLY BONDED MULTI-LAYERED 2D THIN FILMS - AN EXPERIMENTAL AND “AB INITIO” INVESTIGATION

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Surface modification of gold is completed by using the radicals formed through the electrochemical reduction of the heterocyclic diazonium salt dissolved in either acidic aqueous media or organic media. The grafted gold surface is analyzed by using: XPS spectroscopy, AFM, ellipsometry and Raman spectroscopy. As analyzed by AFM the grafted layer covers homogenously the gold surface and has a thickness of about 25 nm (measured both from AFM and ellipsometry). In order to better understand the interface a slab model of Au (111) surface containing a grafted heterocyclic moiety with a 25-angstrom vacuum layer was constructed. This model is used for molecular mechanic calculations from which a number of important data were extracted, such as the geometry of the boned heterocyclic moiety, the interaction of the layer with water molecules, the bond strength of the interface, etc.

Acknowledgements: Erasmus +.

Keywords: diazonium, XPS spectroscopy, ellipsometry.

ICTM P-6

^{1}H NMR STUDY OF THE REACTIONS BETWEEN DINUCLEAR PLATINUM(II) COMPLEXES AND NITROGEN-CONTAINING BIOMOLECULES

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Platinum-based drugs have been widely applied as classical chemotherapeutic agents, especially cisplatin, which the anticancer activity is based on its ability to form intrastrand covalent adducts with DNA by binding of Pt to the N7 atoms of two adjacent guanine bases [1]. In the present study the reactions between biologically relevant ligands such as Ac-L-His-Gly and guanosine-5’-monophosphate (5’-GMP) and dinuclear Pt(II) complexes with general formula $[\{\mathrm{Pt(en)Cl}\}_2(m\text{-}\mathrm{L})]\mathrm{Cl}_2$ (L is pz, 4,4’-bipy, bpa) were studied by ^{1}H NMR spectroscopy. It was found that in the reaction of Ac-L-His-Gly with $[\{\mathrm{Pt(en)(H_2O)}\}_2(m\text{-}\mathrm{pz})]^{4+}$ the regioselective cleavage of the His–Gly amide bond occured. However, in the reaction of this dipeptide with $[\{\mathrm{Pt(en)(H_2O)}\}_2(m\text{-}4,4'\text{-}\mathrm{bipy})]^{4+}$ and $[\{\mathrm{Pt(en)(H_2O)}\}_2(m\text{-}\mathrm{bpa})]^{4+}$ complexes the cleavage of the His–Gly amide bond did not occurred. The reactions of these Pt(II) complexes with 5’-GMP resulted in formation of $[\{\mathrm{Pt(en)}(5'\text{-}\mathrm{GMP}\text{-}N7)\}(m\text{-}\mathrm{L})\{\mathrm{Pt(en)Cl}\}]^{+}$ products. The obtained second-order rate constants (k_2) indicate that $[\{\mathrm{Pt(en)Cl}\}_2(m\text{-}4,4'\text{-}\mathrm{bipy})]^{2+}$ complex shows the best binding ability for 5’-GMP.

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Keywords: dinuclear platinum(II) complexes, N-containing biomolecules, 1H NMR.

ICTM P-7

HYDROLYSIS OF THE AMIDE BOND IN L-METHIONINE-CONTAINING PEPTIDES CATALYZED BY NEW DINUCLEAR Pt(II) COMPLEXES WITH AROMATIC 1,5-NAPHTHYRIDINE BRIDGING LIGAND

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Recent years have witnessed an increasing interest in the study of interactions of methionine-containing peptides with different Pt(II) complexes which were found as effective catalyst for the hydrolytic cleavage of these peptides. In general, it was shown that platinum(II) complexes spontaneously bind to the heteroatom in the side chain of L-methionine and promote cleavage of the amide bond involving the carboxylic group of the anchoring amino acid [1]. As a continuation of this investigation, in the present study, new dinuclear Pt(II) complexes, $[\{\mathrm{Pt(L)Cl}\}_2(m\text{-}1,5\text{-nphe})](\mathrm{ClO_4})_2$ (1,5-nphe=1,5-naphthyridine ligand; L is ethylenediamine (en), 1,3-pentanediamine (1,3-pnd) and 2,2-dimethyl-1,3-propylenediamine (2,2-diMe-1,3-pd)) have been synthesized and characterized by elemental microanalysis, NMR (^{1}H and ^{13}C), IR and UV-vis spectroscopy. The chlorido Pt(II) complexes were converted into the corresponding aqua species, $[\{\mathrm{Pt(L)(H_2O)}\}_2(\mu\text{-}1,5\text{-nphe})]^{4+}$ and their reactions with Ac-L-Met-Gly were studied by ^{1}H NMR spectroscopy. All reactions were performed in 1:1 molar ratio in the pH range $2.0 < \mathrm{pH} < 2.5$ at 37 °C in D_2O as solvent. It was found that in all investigated reactions regioselective cleavage of the Met-Gly amide bond has occurred. We found that the rate of the hydrolyses depends on the steric bulk of bidentate coordinated diamine ligand in the dinuclear platinum(II) complexes.

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Acknowledgements: Financial support by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172036) is gratefully acknowledged.

Keywords: dinuclear Pt(II) complexes,1,5-naphthyridine, L-methionine-containing peptide.

ICTM P-8

EXAMINATION OF THE NATURAL MATERIAL PERLITE FROM THE REPUBLIC OF MACEDONIA AND ITS APPLICATION FOR THE SYNTHESIS OF ZEOLITE 4A

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The Republic of Macedonia has a large number of non-metallic raw materials that can be used to obtain new products that offer a variety of applications. One of these raw materials is the perlite of the Kavadarci region of the Republic of Macedonia. Perlite represents volcanic glass. The components of the perlite are: quartz, plagioclass, K-feldspat, biotite, muscovite and in small amounts zirconium, chalcopyrite and apatite. This material origins from magmatic rocks. The obtained chemical analysis show that SiO_2 is dominant oxide with 75.47 mass% and Al_2O_3 12.77 mass%. and small amount of Fe_2O_3, 0.94 mass%. The water content is in the range of 2-5%. The perlite has crystalline structure, proved by IR- analysis and X-ray. This paper examines the structure and thermal transformations of perlite, with the possible application of the synthesis of zeolite 4A. The results will be displayed in tabular and graphic.

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Keywords: perlite, chemical analysi, structural method, synthesis, zeolite 4A.

ICTM P-9

ADSORPTION CHARACTERISTIC OF THE RESIDUE EXTRACTED WITH 10% HCl SOLUTION FROM NATURAL RED OPALITE AGAINST WATER VAPOR DEPENDING ON THE PARTICLE SIZE

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The material that is taken for examination is from the site "Gorni Stubol" in Probistip. From the chemical analysis we can conclude that the raw material is with a pinkish – red color resulting from a large amount of Fe_2O_3 oxide (12.80%). The chemical activation of the red opalite was carried out with a 10% solution of HCl to a Fe_2O_3 content of 2.24%. The chemical analysis and granulometry composition of the residue is given tabular. For our tests was taken material with particle sizes over 0.063 mm and 0.063 mm below. The absorption characteristics were investigated by a static – gravimetric method. The obtained results will be shown graphically with the B.E.T. adsorption isotherms and their linear forms. Certain specific surfaces of the linear forms are $S = 3.92\ m^2 / kg * 10^3$ and $S = 37.01\ m^2 / kg * 10^3$.

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Keywords: adsorption, red opalite, chemical activation, B.E.T equation, specific surface area.

ICTM P-10

BIOCOMPATIBLE MAGNETIC COLLOIDS: INSIGHT INTO THE STRUCTURE, MORPHOLOGY AND INFLUENCE OF EXTERNAL MAGNETIC FIELD

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Cobalt ferrite ($CoFe_2O_4$) particles have been prepared in nanocrystalline form by several techniques (hydrothermal synthesis, ultrasonic assisted synthesis, microemulsion synthesis, mechanochemical synthesis and microwave synthesis). All samples were coated with starch to find biomedical applications in the field of drug delivery, MRI and hyperthermia. Cobalt ferrite is chosen because its high magneto-crystalline anisotropy that originates from the spin-orbit coupling at crystal lattices. The synthesized coated and uncoated nanoparticles were characterized by X-ray powder diffraction (XRPD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Light transmitting measurements of laser beam of 655 nm propagating through starch coated $CoFe_2O_4$ nanoparticles, under the influence of an external magnetic field, were presented.

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Keywords: ferrofluids, starch coating, cobalt ferrite.

ICTM P-11

KINETICS OF THERMAL DECOMPOSITION OF RARE-EARTH SELENITES

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By precipitation in aqueous solution the rare-earth selenites $Ce_2(SeO_3)_3×3H_2O$, $Nd_2(SeO_3)_3×5H_2O$, $Sm_2(SeO_3)_3×5H_2O$ and $Er_2(SeO_3)_3×3H_2O$ were obtained and characterized using TG/DTG/DTA analysis. On the basis of the thermogravimetric curves the kinetic of the dehydration and decomposition of the selenites was studied. Several mathematical models were used to describe the processes as well as eight different calculation methods.

The dehydration of the selenites $Ce_2(SeO_3)_3×3H_2O$, $Nd_2(SeO_3)_3×5H_2O$ and $Sm_2(SeO_3)_3×5H_2O$ proceed in one step about 200-250°C while this for $Er_2(SeO_3)_3×3H_2O$ in two steps at the temperature intervals 80–230°C and 250–330°C. The decomposition of the anhydrous selenites $Nd_2(SeO_3)_3$ and $Sm_2(SeO_3)_3$ showed a small weight loss and a strong exothermic peak which is related to the simultaneous disproportionation of the selenite and its conversion to the selenate, and the reduction of the formed selenate with evolved of oxygen.

Similar behavior is not occurred in decomposition of other selenites. An exothermic effect (430°C) without weight loss is occurred at the decomposition of anhydrous $Er_2(SeO_3)_3$, which due to recrystallization of the selenite and it transformation to other polymorphic modification.

The decomposition of $Ce_2(SeO_3)_3$ to Ce_2O_3 proceed without formation of intermediate stable phases. The other selenites $Nd_2(SeO_3)_3$, $Sm_2(SeO_3)_3$ and $Er_2(SeO_3)_3$ gradually decomposed to oxoselenites by the type $R_2O(SeO_3)_2$ and $R_2O_2SeO_3$.

The kinetic parameters – the values of activation energy, pre-exponential factor in the Arrhenius equation, change of entropy, enthalpy and Gibbs free energy were calculated for the formation of active complex by the reagent.

Keywords: Rare-earth selenites, thermal decomposition, kinetic parameters.

ICTM P-12

STRUCTURAL AND ELECTRONIC PROPERTIES OF $Hf(SeO_4)_2(H_2O)_4$: A COMBINED X-RAY AND QUANTUM MECHANICAL STUDY

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Hafnium selenate was obtained using the method of hydrothermal synthesis. A single crystal of dimension 0.1 x 0.07 x 0.05 mm^3 was selected and X-ray intensity data was collected at a temperature 290 K on Enraf-Nonius CAD4 diffractometer. The selenate cristallizes in the orthorhombic crystal system, with space group Fddd and lattice parameters obtained are: a = 5.6431(4) Å, b = 11.9463(6) Å, c = 26.5207(14) Å, $\alpha = \beta = \gamma = 90.00°$, V = 1787.87(18) Å^{3}and Z = 8. In this structure, the Hf^{4+} ion, surrounded by eight oxygen atoms that belong to two SeO_4^{2-} ions and to four water molecules.

The molecular geometry optimization and all quantum chemical calculations (converged to 10^{-8} a.u.) were performed by using the hybrid B3LYP method. The geometry optimization was performed by means of 6-311+G(d,p) basis set and LANL2DZ for Hf atom. The optimized structural parameters were used in the vibrational frequency calculations at the DFT level to characterize the stationary point as minima. The absence of imaginary frequencies in the calculated vibrational spectrum confirms that the structure corresponds to minimum energy. The energy of Homo and Lumo molecular orbitals, the global reactivity descriptors and molecular electrostatic surface potential (MESP) were obtained to get better insight on charge density distribution. The large Homo-Lumo energy gap indicates a high kinetic stability of compound. The vibrational frequencies of the fundamental modes of the compound were precisely assigned, analyzed and the theoretical results were compared with the experimental one.

Keywords: X-ray crystal structure, DFT, Hafnium selenate.

ICTM P-13

REACTIVITY OF COPPER(II) COMPLEXES OF S-ALKYL DERIVATIVES OF THIOSALICYLIC ACID TOWARD SMALL BIOMOLECULES, CALF THYMUS DNA AND BOVINE SERUM ALBUMIN

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Among transition metal ions copper is known as an endogenous metal for humans, with characteristic biological redox activities and relatively strong affinity for nucleobases. Copper complexes exhibit their antitumor activity on few differente ways, they generate a high amount of ROS, which causes oxidative damage to mitochondria and biomacromolecules. Copper(II) complexes have been reported to have moderate to good binding affinity with DNA, mostly via intercalation [1].

A few copper(II)-complexes of S-alkyl derivatives of thiosalicylic acid were used to exam the reactivity toward small biomolecules.These measurements showed that the synthesized complex has a good affinity toward studied ligands. The interaction of this metal complex to calf thymus DNA (CT-DNA) and bovine serum albumin (BSA) was further examined. Overall, the studied complex exhibited good DNA and BSA interaction ability.

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ICTM P-14

SYNTHESIS AND CHARACTERIZATION OF COPPER(II)-COMPLEXES WITH S,O-TETRADENTATE LIGAND

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Complexes of copper(II) can have remarkable potential for the expression of antimicrobial, antiviral, anti-inflammatory, and cytotoxic activity [1]. Thiosalicylic acid and its derivatives have a variety of applications, from the treatment of inflammatory, allergic and respiratory diseases to potential applications in the prevention of cirrhosis of the liver and in investigation of the contact sensitivity of drugs.

In this work we report synthesis and characterization of S,O-tetradentate ligand, derivative of thiosalicylic acid and corresponding copper(II)-complex.

S,O-tetradentate ligand, derivatives of thiosalicylic acid, were prepared by alkylation of thiosalicylic acid with the corresponding alkenyl dihalogenide in alkaline water-ethanol solution. The corresponding complexes were obtained by direct reaction of copper(II)-nitrate with the ligand precursor in molar ratio 1:1 with addition of equimolar amount of lithium-hydroxide in aqueous solution with satisfactory yields (more than 80%). The Obtained compounds were characterized by microanalysis, UV-Vis, infrared, and NMR spectroscopy.

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ICTM P-15

INFLUENCE OF AMINOACIDS ON THE CHARACTERISTICS OF DOUBLE DOPED CALCIUM PHOSPHATE PRECURSORS

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In the present study the effect of the lower aminoacids glycine, alanine and valine, naturally present in the biological matrices, on the chemical composition, phase composition and morphology of biomimetically synthesized calcium-phosphate precursors doped with Mg^{2+} and Zn^{2+} ions, is studied. The experiments are performed with dilute solutions (buffers with acid concentration of 7 g/L) and concentrated solutions of the acids (220 g/L of glycine, 140 g/L of alanine and 60 g/L of valine), leading to a change in the rheology of the medium.

Keywords: calcium phosphates; aminoacids; biomimetic syntesis.

ICTM P-16

APPLICATION OF k_0-INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS FOR DETERMINATION OF MAJOR AND TRACE ELEMENTS IN SOME MANGANESE MINERALS

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Major, minor, and various trace elements contents in three manganese minerals, from Republic of Macedonia, were determined. The studied minerals belong to the carbonate group [kutnohorite, $CaMn^{2+}_{0.6}Mg_{0.3}Fe^{2+}_{0.1}(CO_3)_2$ (from Sasa)] and to the inosilicate subgroup [carpholite, $Mn^{2+}Al_2Si_2O_6(OH)_4$ (from Vrbsko); rhodonite, $Mn^{2+}_{0.9}Fe^{2+}_{0.02}Mg_{0.02}Ca_{0.05}SiO_3$ (from Sasa)]. Carousel facility of the TRIGA Mark II research reactor for irradiation and multielement technique k_0-instrumental neutron activation analysis (k_0-INAA) for element concentrations was used. In total, thirty-eight various elements were determined in the investigated minerals by short, intermediate/medium and long half-life radionuclides. The content of As, Co, Ga, K, Na, Sc and Zn in carpholite, of As, K, Na, Ta, W and Zn in rhodonite and of Sr in kutnohorite was found to be higher compared to the other investigated trace elements. It was found that kutnohorite contains lower amounts of trace elements.

Keywords: carpholite, rhodonite, kutnohorite, Macedonia, k_0-INAA.

ICTM P-17

X-RAY AND NEUTRON DIFFRACTION STUDY OF $YCo_{1-x}Cr_xO_3$ (x = 0.25, 0.5, 0.75) PEROVSKITES SYNTHESIZED BY SOLUTION COMBUSTION METHOD

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Perovskite compounds with nominal composition $YCo_{1-x}Cr_xO_3$ (x = 0.25, 0.5, 0.75) were synthesized by solution combustion method using urea as a fuel. The as-prepared samples were additionally heated at 800 ºC for 4 hours. The X-ray diffraction analysis showed that all compounds are single phase with orthorhombic perovskite structure. The unit cell parameters and cell volume increase with the increase of chromium content. Neutron diffraction measurements within the temperature region 300 - 1.5 K show that unit cell parameters and cell volume decrease with the decrease of the temperature. Magnetic ordering appeared at temperatures 20 K, 85 K, 120 K for x = 0.25, 0.5 and 0.75 respectively. The refinements of the crystal and magnetic structures for samples at 1.5 K reveal G5 type magnetic ordering. It was confirmed that Co^{3+} ions in these structures are in low spin state.

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ICTM P-18

SEVERAL ASH FEATURES OBTAINED FROM RICE HUSK

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Annual production of rice in the Republic of Macedonia is 19 000 - 35 000 t, bearing in mind that about 22% of the mass belongs to rice husk. Even though rice husk is rich with silica and has high caloric value, in our country is treated as a waste, its disposal is serious problem for processors.Rice husk ash (RHA) is one of the most silica, rich raw material containing about 85-95% silica after a complete combustion. In the past, combustion was the only way rice processors handled it, without taking into account the consequences for the environment. Certain quantities of ash obtained by uncontrolled combustion exist at the landfills. In this work characteristics at RHA, obtained by uncontrolled combustion are examined.It is a snow-white powder with a low density (about 130 kg / m^3), and the dimensions of the particles are between 10 and 200 microns (measured by laser granulometry). Compared with the density of a sand, silica particles with similar dimensions is 1460 kg/m^3 which indicates a highly porous structure of RHA. X-ray diffractograms and FTIR spectra indicate an crystal silica structure. X-ray fluorescence spectra, show the large presence of Silicon, and small quantities of Aluminum and Iron in RHA.These characteristics of RHA gives opportunity for its use as filler absorbents and further processing in more sophisticated and high cost silica materials.

Keywords: rice husk, combustion, ash.

ICTM P-19

APPLICATION OF NATURAL TUFFS IN THE PROCESSES OF PURIFICATION OF GRAPHICAL INDUSTRY WASTE WATER

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Graphical industry waste water contains, in addition to heavy metals (pigments), also dryers and mineral oils, resins, additives, binders, etc, and as such may not be discharged into the natural recipients. This study represents an attempt to find a more economical and better method of waste water purification in the laboratory conditions. Since adsorption is one of the methods of waste water purification, the study spectrophotometrically examined the chemical oxygen demand (COD) before and after adsorption of graphical industry waste water on the zeolite materials – tuffs, the deposits of which are located in the rock joints of the serpentine zone in the region of the Republic of Srpska (Bosnia and Herzegovina). The results obtained were compared with the results of adsorption on the referential adsorbent – activated carbon. Based on the obtained results, the efficiency of COD decrease in the waste water was calculated, which proved that white tuff had produced good results (from 35% to 75%). As expected, those results were worse than the ones with the activated carbon. Adsorption of waste water with tuffs may be also used in the combination with some of standard methods in the process of purification, such as filtration. Namely, experimental research shows that there is a contribution to the COD decrease by 10 to 60% compared with the waste water purification process only with filtration, without a previous tuff adsorption.

Keywords: adsorption, zeolites, tuff, waste water.

ICTM P-20

CHEMICAL, SPECTRA-STRUCTURAL AND MICROSCOPY STUDY OF THE NATURAL TRIDYMITE FROM REPUBLIC OF MACEDONIA

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The naturally occurring tridymite collected from Kavadarci region, Republic of Macedonia represents a pretty loose, soft, weak rock with white to greyish color that resembles diatomaceous earth. The chemical composition of the samples was determined by classical silicate analysis and the results revealed presence of the following oxides (wt%): SiO_2 (90.17), Al_2O_3 (1.79), Fe_2O_3 (0.328), MnO (0.0004), TiO_2 (0.055), CaO (0.132), MgO (0.20), K_2O (0.52), Na_2O (0.25), and LOI (6.15). Results from the X-ray diffraction examination enabled to determine presence of predominant tridymite crystalline phase, associated with quartz and muscovite. The IR spectrum of the naturally occurring tridymite exhibits absorption bands at 791 cm^{-1} and 1100 cm^{-1} ascribed to the stretching Si–O–Si vibrations. The band at 3650 and 1640 cm^{-1} are assigned to the stretching and bending vibrations from the absorbed water, respectively. Characteristics hexagonal crystals of tridymite and globular forms present in the raw material were found from the SEM investigations.

Keywords: natural tridymite, XRPD, FTIR, SEM.

ICTM P-21

NEW OPTIMIZED TWO-STEP LIQUID-LIQUID EXTRACTION METHOD FOR CONSECUTIVE ELIMINATION OF THALLIUM AND ARSENIC AS MATRIX ELEMENTS IN LORANDITE MINERAL

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In the process of screening of the content of trace elements, in minerals or in other inorganic compounds, their limit of detection is raised and determination is often questionable and even impossible due to the interference of the minerals' matrix elements. Thus, some valuable trace elements can remain undetected that lowers the estimation for the possible economic exploration of the geological deposit or locality. Lorandite mineral, $TlAsS_2$, is even more intriguing and important for fundamental scientific investigations because it can be used to determine the neutron flux from the sun [1]. Thus, the principal goal of this research was to find a suitable, cheap, reliable, and fast method to selectively and consecutively eliminate thallium and arsenic and lower the limit of detection for determination of the present trace elements. The method was based on the separate optimization of the molarity of HCl as well as the volume of organic solvents including diisopropyl ether, diethyl ether, *n*-amyl acetate and isoamyl acetate. The optimized HCl concentration enabled extraction of thallium (as chloride complex) and its migration to the organic top-layer. At first, thallium(I) nitrate was used by adding realgar (As_4S_4) to simulate the composition matrix for lorandite since the latter mineral is very rare and valuable to be used for optimization. In addition, multielement standard simulate (Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mo, Ni, Pb, Sr, Tl, V, Zn) solution was used to simulate the possible present trace elements. Once all conditions were optimized, two-step consecutive liquid-liquid extraction selecting *n*-amyl acetate (to eliminate Tl) and toluene with KI (to eliminate As) was applied for the dissolved lorandite. Determination of all elements was performed using ICP-AES and the results were correlated with those obtained for untreated, pure loranditel.

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Keywords: Thallium/arsenic matrices, liquid-liquid extraction, trace elements, lorandite.

Organic Chemistry, Biochemistry and Pharmaceutical Chemistry (OBPC)

OBPC O-1

THE EFFECT OF A HIGH CONCENTRATION OF POLLUTANT ON METABOLIC ACTIVITY OF SELECTED FUNGI AND THEIR BIOREMEDIATION POTENTIAL

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Not presented.

OBPC O-2

SYMMETRICAL AND UNSYMMETRICAL NCN-COORDINATING LIGANDS BASED ON PYRENE STRUCTURE - SYNTHESIS AND CHARACTERIZATION

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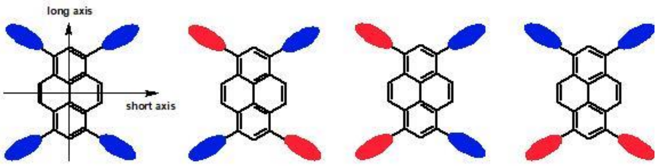
In recent decades a great interest has been shown in the research area of exploring, designing and finally synthesizing of more efficient materials for specific application.[1] The part of new materials due to the interesting photophysical and chemical properties can be successfully used in itself as new materials in electronic devices, for example organic light-emitting diodes (OLEDs) or can be substrates in synthesis of other materials which can be applied in the other part of industry such as electrochromic uses, information storage, and molecular wires.[2,3] The group of compounds which exhibits above-mentioned properties are pyrene derivatives, especially NCN-cyclometalated pyrenes substituted in positions 1, 3, 6, and 8.[4] This is due to the highly π-conjugated system of pyrene core, good thermal stability, promising charge-carrier mobility and hole injection ability. Only functionalized pyrenes can be exploited as a blue-light emitter because of the tendency of this molecules to π-stacking and form excimers in condensed media is much lower than for unsubstituted pyrene. Modification of the chemical structure of pyrene, particularly in the active region (1, 3, 6, 8-positions) can provide materials with excellent operating parameters, including a real reflectivity of display colors, flexibility, and resistance to mechanical stresses.



In this work, I present novel derivatives of pyrene substituted at positions 1, 3, 6, 8 with different heteroaryl groups which were obtained by cross-coupling and cycloaddition reactions. Heteroaryl groups are substituted to provide the short axial symmetry and asymmetry to target compounds. What is worth to emphasize, NCN-cyclometalating ligands having a center of symmetry have been described in the literature insignificantly whereas unsymmetrical pyrene ligands are completely unknown. All obtained molecules were thoroughly characterized. The structures of all obtained compounds were confirmed by ^{1}H, ^{13}C NMR, and HRMS. What is more, detailed characterization by UV-Vis spectroscopy, absorption, and emission spectra were recorded. Thermal properties were checked by using TGA. Theoretical studies: density functional theory DFT and time-dependent density functional theory TD-DFT were conducted to deeper understanding the experimental results.

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Keywords: pyrene, organic synthesis, photophysical properties.

OBPC O-3

NOVEL PHENOTHIAZINE DERIVATIVES - SYNTHESIS AND CHARACTERIZATION

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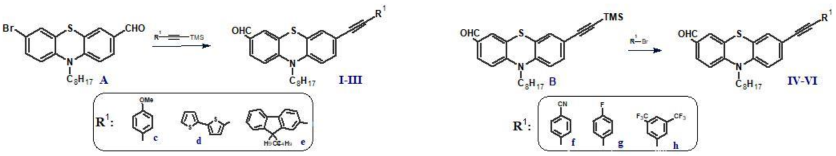
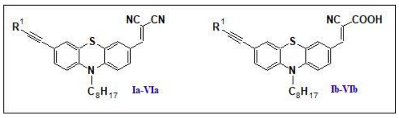
Phenothiazine and its derivatives are a very appealing family of sulfur-nitrogen heterocycles that can be applied in many versatile fields. Phenothiazine and particularly its substituted derivatives are well-known for their wide range of biological and pharmacological activities [1]. Recently, phenothiazine derivatives have been synthesized in the context of D-A systems where act as a strong electron-donor unit. The synthesis of new compounds based on donor-acceptor (D-A) system has attracted significant interest and became important approach target for scientists in recent years. The D-A molecules are widely applied as materials in organic electronics as photovoltaic cells and emissive layers in organic light-emitting diodes (OLEDs) [2].



Scheme 1



Scheme 2

We present the synthesis and investigation of novel D-A system based on phenothiazine framework. In the first step intermediates A, B and c-e were synthesized in multistep reactions (Scheme 1). The novel 7-arylsubstituted 10-octyl-10*H*-phenothiazine-3-carbaldehydes (I-VI) were obtained via Sonogashira Pd-catalyzed cross-coupling reaction of A and B with protected by TMS group ethynyl arenes (c-e) and bromoarenes (f-h) with good yield (56-87%). Finally, the unsymmetrically functionalized phenothiazines (I-VI) were converted to Ia-VIa and Ib-VIb by the Knoevenagel condensation reactions with malononitrile and cyanoacetic acid. The novel compounds were fully characterized by spectroscopic methods (^{1}H NMR, ^{13}C NMR, HRMS). In addition, the photophysical properties of phenothiazine derivatives were thoroughly investigated and confronted with theoretical calculations. The photophysical properties of presented compounds imply that they are very promising D-A materials for various applications.

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Acknowledgements: This work was supported by the National Science Centre of Poland (Project OPUS-11 No 2016/21/B/ST5/00805).

Keywords: phenothiazine, organic synthesis, characterization.

OBPC O-4

DESIGN OF IN VIVO STABILIZATION TECHNIQUE FOR LIPOSOMAL NUCLEIC ACIDS` DELIVERY SYSTEMS

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Molecular therapy, including gene therapy, is a promising strategy for the human diseases treatment. It is known that DNA and RNA molecules are not able to penetrate into cells for providing their biological effect, so using vectors for their delivery is necessary during drug design. The most attractive strategy is to use cationic liposomes for this purpose. Moreover to increase the liposomes circulation time their surface can be modified by polyethylene glycol (PEG), which is able not only to create steric barrier on the particle`s surface and prevent the interaction with blood plasma lipoproteins, but also inhibits the protein adsorption, opsonisation and subsequent degradation in human body. The aim of this work was to evaluate how the PEG addition affects on circulation of lipoplex in blood.

Liposomes preparation (including PEG-modified liposomes) and pharmacokinetic study were performed. For in vivo experiments BALB/c mice were used (6 animals in each group), liposomes were modified with pyren fluorescent label and siRNA was modified with vic fluorescent label for the possibility of their detection in the blood. Lipoplexes were injected intravenously. For time points 0, 2, 5, 10, 20, 30, 45 and 60 minutes were chosen. The concentration of components was evaluated by HPLC method with fluorescent detection.

It was shown that addition of 5% of PEG to liposomal composition by mass can prolong a circulation time of lipoplex in the bloodstream. It should be also noted that the concentration of lipoplex in blood during first 10 minutes is higher for PEG-liposome in comparison with unmodified liposomes. Thus we can assume that pegylation is an attractive approach for prolonged liposomal nucleic acid delivery system design, but the appropriate percentage of PEG addition as well as liposom/RNA ration should be examined.

Acknowledgements: This work was supported by Russian Science Foundation (grant № 17-74-10111).

Keywords: liposomes, PEG, prolonged gene delivery.

OBPC O-5

SYNTHESIS OF HYDROPHOBIC PEG DERIVATIVES FOR LIPOSOMAL NUCLEIC ACIDS DELIVERY

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To inhibit the liposome capture by MPS cells their surface need to be modified with inert molecules that would form a satirical barrier. The most common polymer for this purpose is polyetheleneglycole (PEG). PEG derivatives with hydrophobic anchor would be securely fixed in liposomal bilayer.

Three PEG derivatives with different hydrophobic domains that contained cholesterol, octadecylamine or stearic acid residue were synthesized. These compounds were used in amount of 5 mol. % for modification of liposomal surface based on lipotripeptide OrnOrnGlu(C_{16})$_2$. Biological and physico-chemical properties of prepared liposomes were tested by means of various methods.

Three PEG derivatives with various hydrophobic anchors were synthesized: methoxypolyetheleneglycole$_{2000}$-4-cholesterolesuccinic ester, methoxypolyethelenglycole$_{2000}$-octadecylamide and methoxypolyethelenglycole$_{2000}$-stearic ester. Photon-correlation spectroscopy showed that addition of PEGs increase particle size by 10-15 nm. It was shown that PEG derivatives decrease liposomal aggregation and sedimentation; liposomal dispersions stayed stable for half of year. MTT tests showed that PEGs do not influence on liposomal cytotoxicity. All derivatives had similar properties; however, the synthesis of the one with octadecylamine domain was easier. Transfection activity of liposomes containing this PEG derivative was investigated; the results showed that pegylated liposomes retain a sufficiently high ability for nucleic acids delivery.

Regarding to all conducted assays and compounds design the most balanced compound was the PEG derivative of octadecylamine. Liposomes modified with this compound can be used in *in vivo* experiments.

Acknowledgements: This work was supported by Russian Science Foundation (grant № 17-74-10111).

Keywords: liposomes; PEG; hydrophobic anchors.

OBPC O-6

MULTIPLE EXPERIMENTAL DESIGNS IN OPTIMIZATION OF EXPERIMENTAL VARIABLES IN FORCED DEGRADATION STUDY OF ROSUVASTATIN

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This paper presents optimization of the experimental conditions for forced degradation studies (FDS) of rosuvastatin employing experimental design methodology (DoE). For this purpose, rosuvastatin as a model active ingredient was subjected to stress under acidic, alkaline, oxidative, thermal and photolytic conditions.

Three experimental design types were applied: two-level full factorial design, central composite design and Box-Behnken design. In all designs time of exposure, temperature and stressor strength were selected as investigated factors, while content of rosuvastatin was selected as response to be modeled by DoE methodology.

Quantification of rosuvastatin was performed using optimized and validated RP-*HPLC* method. The chromatographic separation was achieved on Nova Pak C18, 3.9x150 mm i.d; 4 mm maintained at ambient temperature, using isocratic elution with triethylamine buffer (6 mL of triethylamine in 1000 mL of water, pH adjusted to 5.5 with *o*-phosphoric acid), acetonitrile and methanol (59:18:23) as mobile phase. The flow rate was 1.5 mL/min and analyte were monitored at 242 nm.

Despite availability of diverse literature reports that defines the concept of forced degradation, detailed information about a forced degradation strategy is not provided and the experimental conditions to conduct forced degradation are described in a general way without description of the exact stress conditions to be applied [1–9]. Literature review reveals the implementation of DoE and full factorial design concepts for optimization of forced degradation conditions [10–12], but till date, far from our knowledge, no report exists for rosuvastatin as model drug. Therefore, the goal is to investigate the advantages and drawbacks of each design and identify the most convenient solution for the further optimized degradation study.

Detailed statistical evaluation of mathematical models was performed. The studied designs not only differ in the number of experiments but also in quality of information that can be extracted after their application. All three methods were efficient in the statistical modeling and optimization of the influential variables and led to almost the same optimal degradation conditions and predicted amount of formed degradation products. The central composite design and two-level full factorial design created significantly better models compared to Box-Behnken design. As two-level full factorial design requires a smaller number of experiments it was chosen for theoretical examination of experimental space. Multi objective optimization aiming to achieve optimal degradation (5-20%) at minimal analysis time was performed by a grid point search, using desirability plot. The defined optimal degradation was achieved using 0.1M HCl at 25ºC for 15min (acid degradation), 30% H_2O_2 at 25ºC for 15 min (oxidative degradation) and 105ºC for 180 minutes (thermal degradation). Rosuvastatin was shown to be stabile at base degradation so there was no need of prediction.

Thus, we conclude that screening designs appear to be reliable and more economical approach for design of experimental conditions for FDS since they impose a reduction of the amount of time and effort required to conduct the experimental design without losing valuable information. Finally, an improved sample preparation strategy was achieved by application of adequate design.

Keywords: Full Factorial Design, Central Composite Design, Box-Behnken Design, forced degradation, rosuvastatin.

OBPC P-1

CHEMICAL COMPOSITION OF ESSENTIAL OIL FOR THYMUS POPULATION FROM ALBANIA

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This study presents data about chemical composition of essential oils for *Thymus* populations from the Albania. The genus *Thymus* contains about 350 species of aromatic plants in the family Lamiaceae. It is in the form of a beautiful shrub with numerous branches used often as decorative plant besides it uses for culinary and medical purposes. *Thymus* plants are part of spontaneous flora in Albania and almost throughout the Mediterranean areas.

Thymus vulgaris, Thymus capitatus and *Thymus serpyllum* samples from different areas of Albania were taken in July 2017. The air dried plant samples were cut in small pieces (1-2 cm) and after that were subjected to European Pharmacopoeia apparatus (Clevenger type) for 4 hours to obtain *Thymus* essential oil. The chemical composition of essential oils was analyzed using GC/FID technique. The oil of each *Thymus* samples was injected in a Varian 450 GC. VF-1ms capillary column (30 m x 0.33 mm x 0.25 um) were used for separation of compounds. 40-65 compounds were found in analyzed samples.

Para-Cymene, gama-Terpinen, Thymol and Carvacrol were identified as main constituents and all analyzed essential oils of *Thymus* samples from Albania. Para-Cymene was the main constituent for *Thymus vulgaris* samples. Carvacrol was found in higher percentage for *Thymus capitatus* and *Thymus serpyllum*. Thymol was in higher percentage for *Thymus vulgaris* and *Thymus serpyllum*. Total of Thymol and Carvacrol were higher for *Thymus serpyllum*samples. The same compounds were found for all *Thymus* samples but were noted differences in percentage between them. This is related with differences between species obtained for analysis but is not excluded the impact of geographic and geological factors. Data reported in this paper were similar to those published in previous works in Balkan and Mediterranean area.

Keywords: *Thymus*, esencial oil, p-cymene, gama-terpinen, thymol, carvacrol; GC/FID.

OBPC P-2

QUANTUM CHEMICAL STUDIES OF SOME p-SUBSTITUTED BENZOYLHYDRAZONE DERIVATIVES

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Aroylhydrazones and their derivatives are a class of azomethines having the structure Ar–CO–NH–N=CR_1R_2, containing two interlinked nitrogen atoms of different nature and nucleophilic character and a carbon atom which may act as either electrophile or nucleophile according to the reaction environment. In their structure a C=N double bond that is conjugated with a lone electron pair of the terminal nitrogen atom is also presented. These structural ragments are mainly responsible for the physical and chemical properties of hydrazones. Both nitrogen atoms of the hydrazone group are nucleophilic, although the amino typenitrogen is more reactive. The carbon atom of hydrazone group has both electrophilic and nucleophilic character.

Due to their structure hydrazones are important compounds for drug design and they show a broad spectrum of applications in pharmaceutical and industrial fields. These observations increased the need for the development of new hydrazones that possess varied biological activities. Literature studies revealed that hydrazones and various substituted hydrazones are associated with a broad spectrum of biological activities such as antioxidant, antibacterial, antiviral, analgesic, antiplatelet, antimicrobial, and anticancer activities etc. Some derivatives of hydrazones such as nifurtimox (used for the treatment of Chagas' disease) and nifuroxazide (D) (intestinal antiseptic) are marketed. Hydrazones can act as polydentate ligands depending on the nature of the substitution attached to the hydrazone unit. It should also be noted that the complexing properties of hydrazones enhance the potency of drug candidates for these molecules. Hydrzone ligands act synergistically with transition metals to enhance their biological activities.

A group of five *p*-substituted benzoylhydrazone derivatives (**BH**) was previously synthesized in our laboratory. The structural formulas of investigated hydrazones are presented below:

The aim of our work was geometry optimization of investigated **BH** and calculation of: atomic charge, bond length and angle between characteristic atoms in hydrazone molecule, using *Austin Model 1 (AM1)* semiempirical method. The study of the geometry of **BH** is important because of the possible usefulness of such information as an aid to the understanding of mode of action of **BH** as acid as and base and co-coordinative species.

Keywords: p-substituted hydrazone, semiempirical methods, AM1, geometry optimization.

OBPC P-3

THERMODYNAMIC DISSOCIATION CONSTANTS OF SOME BENZOYLHYDRAZONES

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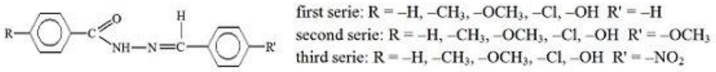
Hydrazones play an important key role in organic, inorganic analytical, heterocyclic and pharmaceutical chemistry. They exhibit a wide range of biological activities such as: antimicrobial, anticonvulsant, antidepressant, anti-inflammatory, analgesic, anticancer, antifungal, antitubercular, antiviral etc. Since the hydrazones have acidic and/or basic functional groups, their ionization state depends on the value of pH of the media, as well as from the values of thermodynamic dissociation constants (pK_{BH^+}). Hence, the subject of this work was determination of pK_{BH^+} values of three series of benzoylhydrazones. The influence of the structure on the pK_{BH^+} values was discussed, too. Structure of investigated hydrazones is as follows:



first serie: R = –H, $–CH_3$, $–OCH_3$, –Cl, –OH R' = –H
second serie: R = –H, $–CH_3$, $–OCH_3$, –Cl, –OH R' = $–OCH_3$
third serie: R = –H, $–CH_3$, $–OCH_3$, –Cl, –OH R' = $–NO_2$

The investigated hydrazones were structurally characterized by UV spectroscopy, infrared spectroscopy (IR), nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) and by elemental analysis. The spectral behavior of investigated hydrazones was followed in perchloric acid media using the methods of UV-Vis spectroscopy. The changes in the UV spectra were used for calculation of dissociation constants (numerically and graphically). The influence of the solvent was eliminated using the method of characteristic vector analysis (CVA). Thermodynamic dissociation constants were determined as an intercept with extrapolation of the curve $pK_{BH^+} = f(\ )$ to zero ionic strength. In order to achieve that, the measurements were performed at three different ionic strengths (0.1, 0.25 and 0.5 mol/dm^3) of investigated solutions.

The pK_{BH^+} values of first series ($–CH_3$) of hydrazones were between 2.56 (–Cl) and 3.44 (–H), the hydrazones of the second series ($–OCH_3$) had values between 3.10 (–OH) and 3.46 ($–OCH_3$) and the pK_{BH^+} values of the third series ($–NO_2$) of hydrazones were from 2.05 (–Cl) to 2.55 ($–CH_3$). The observed differences in the thermodynamic pK_{BH^+} values are probably as a result of the influence of the substituents present in *para* position of the benzene ring.

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Keywords: benzoylhydrazones, dissociation, dissociation constants, thermodynamic pKBH+ values.

OBPC P-4

TOTAL FLAVONOID CONTENT AND RADICAL SCAVENGING ACTIVITY OF RED RASPBERRY (*Rubus idaeus* L.) FRUIT EXTRACTS

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The red raspberry - *Rubus idaeus* L. (family *Rosaceae*) is widely known as *Rubus* species, native to Europe and northern Asia and cultivated in other climate temperate regions. Ethno-medicinal uses of raspberry can be found in many cultures. From ancient traditions, through conventional folk drugs to scientific confirmation of health-promoting components, red raspberry is associated with healing properties. Up-to-date research has identified raspberry as a source of biologically active molecules, such as phenolic acids and flavonoids with a strong capacity to scavenge oxygen radicals. Most of the antioxidative capacity belongs to elagitans, particularly ellagic acid which is almost exclusively in raspberries and according to research shown anti-cancer activity.

The purpose of this study was to examine the influence of extraction method and time of total flavonoids content and the antioxidative capacity of red raspberries (*Rubus idaeus* L.) in southeastern Serbia. Prepared raspberry fruits for extraction under reflux was overflowed with extractant methanol/water/acetic acid (80/19.5/0.5 v/v/v) at the plant material:solvent ratio 1:10 w/v, wherein the time and extraction methods were varied. The bioactive compounds from the prepared reaction mixtures were obtained using reflux extraction at a solvent boiling temperature, by the conventional procedure during 1.5 h and 2.5 h and by ultrasonic extraction method during 0.5 h and 1 h.

The antioxidant activities of the obtained extracts and ellagic acid standard was determined spectrophotometrically using DPPH test. Unlike the ellagic acid standard which at the lower concentrations of the solutions ($2\cdot10^{-4} – 0.1$ mg cm^{-3}) shows the satisfactory antioxidant activity, the extract solutions show the same activity at higher concentrations (0,125-2,0 mgcm^{-3}). The inhibition of DPPH (1,1-diphenyl-2-picrylhydrazyl) radicals was expressed by EC$_{50}$values. The ellagic acid standard ($9,87\cdot10^{-4}$ mg cm^{-3}) showed less value than obtained raspberry extracts (0,219 -0,464 mg cm^{-3}). It can be concluded that the ellagic acid standard has a higher activity of radical scavenging activity compared to the obtained raspberry extracts.

The total flavonoids content was determined using UV-Visible spectrophotometric method and standard procedure. The results were *expressed* as rutin equivalents. The raspberry extract obtained by ultrasonic extraction during 1h showed the highest capacity for neutralizing DPPH radicals and also the highest value of total flavonoids content 9,091 mg g^{-1} of dry extract.

The results of this study showed that red raspberry (*Rubus idaeus* L.) fruit extracts from southeastern Serbia represent a good source of flavonoids with satisfactory antioxidant activity.

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Keywords: *Rubus idaeus* L., extraction, DPPH assay, total flavonoids.

OBPC P-5

ANTIOXIDANT ACTIVITY OF OSAGE ORANGE (*Maclura pomifera* (Raf.) Schneid.) FRUIT EXTRACTS

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Osage orange (*Maclura pomifera* (Raf.) Schneid.) is perennial plant which belongs to Moraceae family and originates from North America. Various Osage orange parts, such as fruit and seed, are used in traditional medicine worldwide for the treatment of sore eyes, tooth pain and uterine haemorrhage. The most abundant Osage orange's compounds are isoflavones pomiferin and osajin. Pomiferin represents the main compound responsible for the antioxidant activity of Osage orange fruit. Beside antioxidant activity, the fruit extracts have antiinflammatory, antiproliferative, anticholinesterase, antinociceptive, antimicrobial and repelent activity. The objective of this study was to determine the yields of extractive matter, as well as chemical composition and antioxidant activities of the Osage orange fruits extracts. The extracts were obtained by maceration using ethanol and acetone at room temperature with solvomodule (ratio of plant material/solvent) 1/4 m/v during 48 hours. Identification of bioactive components in the extracts was performed using HPLC–DAD–ESI–MS analysis. The antioxidant activity of extracts was assessed by DPPH test. The yield of total extractive matter obtained by ethanol and acetone was 9.20 and 6.68 g/100g of fresh plant material, respectively. The following compounds have been identified from the extracts: chlorogenic, neo- and crypto-chlorogenic acids; rutin, pomiferin and isoflavone glycosides. Both extracts at the concentration of 0.20 mg/mlhave neutralized about 80% of DPPH radical. The concentration of ethanol and acetone extracts required to neutralize 50% of the initial concentration of DPPH radical (EC_{50} value) was 80.20 and 81.30 µg/ml, respectively. The presented results suggest that extracts of Osage orange fruits are potential sources of natural antioxidants as an alternative to synthetic additives.

Acknowledgements: This work is a part of the research project "Plant and synthetic bioactive products of new generation" no. TR 34012, financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

Keywords: Osage orange extract, chemical composition, antioxidant activity, HPLC–DAD–ESI–MS analysis.

OBPC P-6

SAFETY ESTIMATION OF TOPICAL APPLICATION OF WILD ORANGE EXTRACT (*Maclura pomifera* (Raf.) Schneid.)

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Maclura pomifera, commonly known as osage orange or wild orange is a perennial plant belonging to the family Moraceae. It originates from the North America. The oil obtained from the seed of this plant is used in traditional medicine for the treatment of various skin diseases. The safety evaluation of different substances after topical application is performing by *in vivo* study with healthy volunteers by measuring the changes of skin biophysical parameters values before and after 24h occlusion. If significant changes in measuring parameters values followed by skin irritation are not occurred, the examined samples should be safe for topical application. Extracts obtained by 48h maceration period of the plant fruits with solvents acetone, n-hexane and ethanol at 1/4 m/w hydromodule and then evaporated to dryness are examined. Dry extracts were dispersed in isopropyl myristate at concentration of 1%. Standard procedure was used for safety evaluation of dry extracts dispersions after topical application. Ten healthy female volunteers were subjected to examination after obtaining the approval of the Ethics Committee of the Medical Faculty in Nis. The samples of extracts dispersed in isopropyl myristate (0.018 g/cm^2) were pippeted to different skin sites on the volar forearms, covered with Parafilm® and cotton adhesive tapes (Sensifix®, Galenika, Serbia). Baseline values were taken prior to the sample application and one hour after the occlusion was removed. Electrical capacitance (EC) of the skin was measured as an indicator of skin hydration, using Corneometer® CM 825 probe. Erythema index (EI) was measured in order to evaluate the skin irritation using Mexameter® MX 18 probe. Probes are parts of Multi Probe Adapter MPA®9 (Courage & Khazaka Electronic GmbH, Germany). The tested samples did not showed statistically significant changes in biophysical parameters values, so it can be concluded that osage orange extracts are safe for topical application.

Acknowledgements: This work is a part of the research project "Plant and synthetic bioactive products of new generation" no. TR 34012, financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

Keywords: topical application, Osage orange extract, biophysical parameters.

OBPC P-7

SYNTHESIS, DESING AND CHARACTERIZATION OF SHORT-CHAIN PEPTIDE ANALOGUES CONTAINING AROMATIC HETEROCYCLIC RINGS

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Bioactive peptides are a specific protein fragments that have a positive impact on body functions and may ultimately influence health. These peptides play an important role in human health. The antihypertensive peptides are one significant group of these peptides, which are used as Angiotensin-converting enzymes (ACE) inhibitors, because they are associated with decreasing of high blood pressure and plays an important role at cardiovascular diseases.

ACE-inhibitors are widely used in the treatment of hypertension by inhibiting the angiotensin converting enzyme responsible for the conversion of angiotensin I to angiotensin II (responsible for vasoconstriction). Various structure activity relationship studies led to synthesis of different kinds ACE-inhibitors[1, 2]. Various structure activity relationship studies led to the synthesis of ACE inhibitors, some are under clinical development.

In this work we present the investigation about synthesis, design and characterization of short-chain peptides with aromatic heterocyclic rings.

The intermediates and small peptide analogues were isolated and characterization by different physic-chemical and spectral methods.

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Keywords: short-chain peptide, ACE, spectral analysis.

OBPC P-8

CHARACTERIZATION OF THE VOLATILE COMPOSITION OF FREQUENTLY USED CULINARY HERBS FROM LAMIACEAE FAMILY (BASIL, MARJORAM, OREGANO, ROSEMARY AND THYME) BY HS-GC-MS/FID

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Food selection and consumption is not only a matter of need, but also a matter of taste and current trends. Spices and culinary herbs necessarily contribute to overall food experience; therefore, their use in food preparation has been an inseparable part of every cuisine since ancient times. The characteristic flavor of spices and herbs results from aroma compounds – more volatile from essential oil and less volatile from oleoresins. Aroma experience and delivery depends on composition of volatiles [1].

This study reports composition of most volatile part of aroma of five commercially available and frequently used aromatic culinary herbs from the mint family, Lamiaceae: basil, marjoram, oregano, rosemary and thyme. Fast headspace isolation (HS) and GC-MS/FID analysis in automated procedure were conducted on 23 samples of culinary herbs purchased in local markets in Niš (Serbia). Qualitative and quantitative composition of HS volatiles is quite different. In HS volatiles of basil samples dominate two compounds: linalool and estragole (mean value±standard deviation=43.8±35.2% and 40.0±33.2%, resp.; number of samples N=7). In case of oregano samples (N=6), carvacrol (23.5±22.2%) and *p*-cymene (20.3±10.6%) are two most abundant volatiles. Despite belonging to the same plant genus, oregano and marjoram samples (N=2) are quite different in HS volatiles composition. Regarding dominant HS volatiles, marjoram samples are characterized by presence of g-terpinene (15.1±1.1%), *trans*- and *cis*-sabinene hydrate (17.3±4.9% and 6.1±0.1%, respectively), sabinene (12.5±0.8%), terpinen-4-ol (12.8±4.2%) and α-terpinene (10.8±1.3%). The leading compound in HS fraction of rosemary samples is eucalyptol (54.3±23.7%; N=5), while *p*-cymene in thyme samples (66.2±19.0%; N=3). Based on the profiles of the HS volatiles, it can be said that the studied culinary plants differ in composition. Additionally, a variability of volatile compounds content depending on the manufacturer was observed. In some cases, variance was within an acceptable range, while in other it was drastic. Therefore, the applied procedure could be applicable in the quality assessment of culinary herbs.

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Keywords: Lamiaceae, culinary herbs, headspace, volatiles.

OBPC P-9

PHYTOCHEMICAL ANALYSIS OF THE *Elaeagnus angustifolia* L. ESSENTIAL OIL AND HEADSPACE VOLATILES

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Elaeagnus angustifolia L., commonly called Russian olive, silver berry, oleaster, Persian olive, or wild olive, or commonly referred to as dafina in Serbia, is a species of *Elaeagnus*, native to western and central Asia, from southern Russia and Kazakhstan to Turkey and Iran. It is now also widely established in Europe and North America as an introduced species. Its fragrant flowers are used in perfume industries. The fruits are edible but they also found application in pharmacy and in folk medicine [1]. The raw or boiled fruit is consumed for the treatment of sore throat, cough, flu, cold, fever, nausea, vomiting, jaundice, asthma, diarrhea and some other symptoms and diseases. Recent pharmacological studies have shown that different parts of *E. angustifolia* L. have anti-inflammatory, antimicrobial, anti-oxidant, anti-mutagenic, analgesic and some other health benefits [2].

Flowers of the plant species *E. angustifolia* was collected in May 2017, at the urban area of the city of Niš. From the fresh specimen, essential oil was isolated by Clevenger type hydrodistillation. The chemical composition of the oil was analyzed by GC-MS, and the content of the volatile components in the native sample by headspace GC-MS. In the essential oil of fresh flowers 52 components were found, what makes 99.3% of present compounds. Headspace analysis showed the presence of 10 components with a share of 99.3% of the total. The major class of compounds, in both investigated specimens, was found to be carboxylic acids and their derivatives with the shares of 93.9% in oil and 91.3% in headspace sample. In particular, just like in previous report [3], the most dominant compound was (*E*)-ethyl cinnamate which accounts nearly 3/4 parts of the essential oil mass. In addition, compounds present in a significant percentage in essential oil (over 3%) were: 2-phenylethyl benzoate (8.4%), (*Z*)-9-ethyl octadecenoate (5.1%) and (*E*)-propyl cinnamate (3.3%). In headspace specimen, the most abundant components were: (*E*)-ethyl cinnamate (61.5%), butanoic acid (15.1%), ethyl benzoate (10.8%) and ethyl hexanoate (3.4%).

Acknowledgments: The authors are grateful to the Ministry of Education, Science and Technological Development for the financial support through the grant No 172047.

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Keywords: *Elaeagnus angustifolia* L., essential oil, headspace volatiles, GC-MS.

OBPC P-10

COMPARISON OF CONVENTIONAL REFLUX AND ULTRASOUND-ASSISTED EXTRACTION TECHNIQUES OF ELLAGIC ACID CONTENT FROM *Rubus idaeus* L.

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In recent times, red raspberries (*Rubus idaeus* L.) becomes important fruit species as rich source of phytochemicals with potential health benefits, especially in mitigating damaging effects of oxidative stress on cells and tissues [1]. Elagitans, particularly ellagic acid almost exclusively found in raspberries, shows anti-cancer activity, according to many researches [2-3]. Novel extraction methods such as ultrasound assisted extraction may shorten the conventional extraction time, decrease the solvent consumption and increase the extraction yield.

Goal of this investigation was analysis of ellagic acid content in red raspberries (*Rubus idaeus* L.) extract obtained from ripe fruts, planted and grown in southeastern Serbia climate, using conventional and ultrasound assisted extraction. Ripe raspberry fruits were extracted under reflux with methanol/water/acetic acid (80/19.5/0.5 v/v/v) as extractant. The conventional and ultrasound assisted extraction were compared on various parameters basis like extraction time and extraction yield. The bioactive compounds were obtained using reflux extraction at a solvent boiling temperature, by the conventional procedure during 1.5 h and 2.5 h and by ultrasonic extraction method during 0.5 h and 1 h. The ellagic acid content was estimated using the UHPLC-DAD-HESI-MS/MS analysis.

By using the ultrasound assisted extraction technique for 0.5 hours, obtained extract contained about 2.5 times higher content of the ellagic acid (0.347 mg/ml) compared to conventional reflux extraction technique/method with for 2.5 h (0.1396 mg/ml). Obtained results in this study showed that for *Rubus idaeus* L. fruit extracts from southeastern Serbia, ultrasound assisted extraction was found to be better than conventional methods as they require less time and give higher content of ellagic acid.

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Keywords: *Rubus idaeus* L., ultrasound-assisted extraction, conventional reflux extraction, UHPLC-DAD-HESI-MS/MS analysis, ellagic acid.

OBPC P-11

METALS CONTENT IN DIFFERENT EXTRACTS OF *Vaccinium myrtillus* L.

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Medicinal plants and their extracts deserve special attention being beneficial for human health. Bilberry (*Vaccinium myrtillus* L.) is classified as a Class 1 herb by the American Herbal Products Association, meaning it can be safely consumed when used appropriately. Although most attention has been focused on flavonoids in relation to health benefits, the investigation of mineral content in different plant parts, and in the corresponding extracts, might be of a great importance as contribution to up to now performed investigations. The content of heavy metals is one of the criteria for the use of plant material in the production of traditional medicines and herbal infusions. Namely, bilberries are rich source of different mineral elements, which are important as essential trace elements or they can be potentially toxic, depending on their concentrations.

The content of sixteen elements including major (Al, Ca, Fe, K and Mg) and trace elements (As, Ba, Cd, Co, Cu, Cr, Mn, Ni, Pb, Sr and Zn) in bilberry fruits and leaves extracts obtained by infusion, maceration and Soxhlet extraction was determined. The processes of maceration and infusion of fruits and leaves were providing the samples MLEM-*Myrtilli folium* and MFEM-*Myrtilli fructus* extracts and MLEI-*Myrtilli folium* and MFEI-*Myrtilli fructus*extracts, respectively. Applying the classical method of continuous, Soxhlet, extraction provided the samples MLES-*Myrtilli folium* and MFES- *Myrtilli fructus* extracts.

The different quantity of metals determined in the investigated extracts might be dependent on the extraction medium. Besides, the duration and temperature of the extraction process highly influenced the metals profile and their quantity. The highest concentration of K, Ca and Mg were detected in MLEI, while the lowest were in MFEM. The concentration of K was from 6.01±0.10 to 17.22±0.02 mg/g, Ca from 0.383±0.005 to 5.94±0.02 mg/g, and Mg from 0.397±0.007 to 3.83±0.02 mg/g. In our study, the concentrations of Mn varied from 42.85±0.10 in MFES to 1210±2µg/g in MLEM, Fe from 5.90 ±0.05 in MFEM to 37.6 ±0.2 µg/g in MFEI, Cu from 1.513±0.010 in MFEI to 33.31±0.09 µg/g in MLES, Zn from 6.281±0.007 in MFEM to 31.48±0.04 µg/g in MLEI, and Cr from 0.123±0.002 in MLEM to 1.11±0.03 µg/g in MLEI.

The permissible limit for toxic metals Cd and Pb in medicinal plants set by World Health Organization (WHO) were 0.3 µg/g and 10 µg/g, respectively, having in a mind that for As limits has not yet been established by WHO [1]. Our study showed that all investigation extracts accumulate these metals below the limits.

Taking that the avarage consumption of leaves/fruits extracts made by infusion/Soxhlet extraction/maceration, and the obtained average yield we took 1g of bilberry fruits and leaves extracts to calculate daily mineral intakes according to the European Economic Community [2]. The presented results revealed that the investigated extracts could be prospective source, not only of antioxidant phenolics, but of Mn, as well, in nutraceuticals/functional food.

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Keywords: bilberry, soxhlet extraction, maceration, infusion, metals content.

OBPC P-12

THE ANTIOXIDANT POTENTIAL OF DIFFERENT EXTRACTS OF *Vaccinium myrtillus* L.

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Vaccinium myrtillus L. (bilberry) was one of the most frequently used antidiabetic remedies of plant origin before the discovery of insulin. In this context, the goal of the study was to establish antioxidant activity of the bilberry fruits and leaves extracts obtained by infusion, maceration and Soxhlet extraction. Taking into account that water herbal infusions are most often used for preparation of traditional phytopreparations during times of illness, but according to the fact that industrial scale production usually underwent with ethanol as solvent we also used Soxhlet extraction as a model method of a complete exhaustion of plant material. In addition, having in a mind that Soxhlet extraction requires high temperature, what might be disadvantage for the thermolabile substances, the maceration was employed, as well, as extraction on ambiental temperature. The processes of maceration and infusion of fruits and leaves were providing the samples MLEM-*Myrtilli folium* and MFEM-*Myrtilli fructus* extracts and MLEI-*Myrtilli folium* and MFEI-*Myrtilli fructus* extracts, respectively. Applying the classical method of continuous, Soxhlet, extraction provided the samples MLES-*Myrtilli folium* and MFES- *Myrtilli fructus* extracts.

To evaluate the antioxidant properties, two different assays were employed to avoid the possible incorrectness in the interpretation of the obtained results regarding the antioxidant properties of the investigated extracts, having in a mind the difference in their working principles. The antioxidant potential of all extracts was evaluated using DPPH and FRAP tests. DPPH assay is based on the hydrogen donating capacity to scavenge DPPH radicals, while FRAP assay is an electron transfer-based test measuring the substance ability to reduce Fe^{3+} to Fe^{2+} (results were expressed as mmol Fe^{2+}/g of extracts used). The ethanol extracts compared to water extracts had a higher antioxidant activity measured by DPPH assay. IC_{50} of the ethanol leaves extracts ranged from 2.92 to 11.94 µg/ml for MLES and MLEI, respectively. The fruits extracts had IC_{50} values in the range of 50.82 to 105.46 µg/ml, for MFEM and MFEI, respectively. The investigated fruits extracts had lower antioxidant potential measured by the employed tests in comparison to leaves extracts. In the case of FRAP assay, the lowest values was for MLEI (0.0011mmol/g) and the highest for MLEM (0.0030 mmol/g), while in fruits extracts the FRAP values ranged from 0.0003 mmol/g for MFES to 0.0014 mmol/g for MFEM.

For estimation of antioxidant activity of ethanol and water extracts of the samples cyclic voltammetry was employed, as well. All samples provided one well defined oxidation peaks in potential window between 0 and 1.2 V at interestingly high potential. Absences of corresponding cathodic peaks were observed. The highest antioxidant capacities were found in the samples labelled as MLEI, MLEM and MLES which was in good accordance with DPPH. Contrary, lowest results from electrochemical measurements were obtained for samples MFES and MFEM. Electrochemical measurements for sample MFEI revealed middle antioxidant capacity value. This was not in accordance with other test measurements what might be explained by nature of the sample and selection of used tests.

Keywords: *Vaccinium myrtillus*; Soxhlet extraction, maceration, infusion; antioxidant activity; cyclic voltammetry; DPPH, FRAP.

OBPC P-13

IN VITRO INHIBITION OF COLLAGENASE BY VARIOUS PEPTIDES, AMINO ACIDS AND CHEMICAL SUBSTANCES

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Matrix metalloproteinases (MMPs) are a family of zinc dependent extracellular matrix (ECM) remodelling endopeptidases having the ability to degrade almost all components of ECM and implicated in various physiological as well as pathological processes. MMPs play an important role in ECM remodeling [1]. Collagenase (EC 3.4.24.3) is transmembrane zinc endopeptidase enzyme, which belongs to the family of MMPs. Collagen is the major structural protein in human skin and plays an important role in many processes including tissue remodeling during development, tissue homeostasis and repair after wounding. Over activation due to photoaging and chronical aging leads to alterations in the collagen composition of the ECM and results in wrinkles, laxity, sagging and a coarse appearance of the human skin [2]. In our study, we have examined collagenase enzyme inhibitory activities of different peptides and amino acids such as glutathione, glycylglycine, cysteine, proline and chemical substances such as tartaric acid, catechin, resorcinol, gallic acid, glycolic acid, and quercetin. Collagenase inhibitory activities of different amino acids and chemical substances were increasing in a dose dependent manner. As obtained results among the studied peptides, amino acids and chemical substances glutathione, cysteine and tartaric acid showed the highest inhibitory activities. It was found that these peptides, amino acids and chemical compounds are potential sources of collagenase inhibitors and may be appropriate to be used as an additional support in pharmaceutical and cosmetic industry.

Acknowledgements: This work was supported by Scientific Research Projects Coordination Unit of Istanbul University. Project number: T-19731.

Keywords: collagenase, vitamins, amino acids, chemical substances, inhibition.

OBPC P-14

INVESTIGATION OF INHIBITORY EFFECTS OF SOME VITAMINS, AMINO ACIDS AND PEPTIDES ON MYELOPEROXIDASE ACTIVITY

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Myeloperoxidase (MPO, EC 1.11.2.2) is an important member of the haem peroxidase - cyclooxygenase superfamily. This enzyme is physiologically expressed in circulating neutrophils, monocytes and some tissue macrophages including microglia and play an essential role in the antimicrobial and antiviral system of humans. MPO is involved in cardiovascular, inflammatory, neurodegenerative, kidney and immune-mediated diseases and therefore nowadays research on MPO inhibitors has been intensified [1-2]. In our study, we have examined MPO enzyme inhibitory activities of vitamins such as ascorbic acid, DL-α-tocopherol, lipoic acid, pyridoxal-5'-phosphate, DL-methionine methylsulfonium chloride, nicotinamide, β-carotene, routine hydrate, riboflavin and anorine hydrochlorid, and amino acids and peptides such as L-cysteine, L-lysine, L-glutamic acid, L-methionine, L-alanine and reduced glutathione. In our study, it was observed that inhibition increased with increasing concentration of chemical substances. According to obtained data it was determined that in the studied vitamins, the highest MPO enzyme inhibition was shown in ascorbic acid with $IC_{50} = 0.01 \pm 0.003$ mM and in amino acids with $IC_{50} = 1.09 \pm 0.73$ mM rate L-cysteine, respectively. As a result it can be suggested that using appropriate chemical substances at right concentatrations show high MPO inhibitory effect.

Keywords: myeloperoxidase, vitamins, amino acids, inhibition.

OBPC P-15

THE CHEMICAL CHARACTERIZATION OF *Salvia officinalis* OIL AND PROPOSAL FOR A PHARMACEUTICAL USE, IN THE FIELD OF SKIN ANTIAGING

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The antiaging properties of essential oil extracted from *Salvia officinalis* have captured the researcher's attention, because of an hypotetical anti-aging effect. It is known that *Salvia officinalis*, as well as other aromatic herbs, is cited as an important antioxidant and anti-glycation source. The anti-glycation effect is essential in skin antiaging field, because it stops the tendency towards the process of collagen stiffening [1]. In this present study, the chemical extraction and analysis of *Salvia officinalis* oil was performed at Banat`s University of Agricultural Sciences, by using GC. Then the data were compared and confirmed by those already existing in other studies [2]. Thus, 38 components were identified in volatile oil extracted from *Salvia officinalis*. The chemical composition shows that oxygenated monoterpenes (camphor, 1,8-cineol, α-thiona and borneol) are in the highest proportion. Camphor is a dominant component (20.64%), followed by eucalyptus (11.75%), borneol (8.80%) and α-thion (8.64%). Hydrocarbon monoterpenes are also in remarkable concentration (α-pinen 9.59%, β-pinen 5.04%). We have proposed and then realized a pharmaceutical form containing different concentrations of salvia oil. The cream was tested by using corneometry (Courage – Khazaka Electronic corneometer), after daily applications on 15 subjects. The entire study lasted 5 weeks, during which each patient was evaluated weekly. The obtained results were centralized and statistically processed using the StatPad application. So we can conclude that that the use of creams that contain sage oil leads to an increase in the skin hydration degree both in the cases of cronoaging and in those of photoaging.

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DOI: 10.1080/14786410500528478

Keywords: *Salvia officinalis*, composition, skin application.

OBPC P-16

CHEMICAL CHARACTERIZATION AND PROPOSAL OF A DERMATOCOSMETIC FORMULATION FOR *Anethum graveolens* ESSENTIAL OIL, FROM TIMIȘ REGION, ROMANIA

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The idea of studying the volatile oil of *Anethum graveolens*, with its applications in in the antiaging cosmetic field, is not at all strange to current trends. A number of beneficial effects have been highlighted, in turn. At least theoretically, about *Anethum graveolens* (*Umbeliferae*) we know that it has a phytoestrogenic effect, but other some add other properties: hepatoprotective, antimicrobial, hypoglycemic [1]. On the other hand, current chromatographic research highlights an interesting composition of the dill volatile oil, comparable to those for which beneficial cutaneous effects have been already demonstrated [2]. The aim of the study were (1) to evaluate the chemical composition of *Anethum graveolens* essential oil, collected from the western side of Romania, (2) after its incorporation into some cutaneous pharmaceutical forms, to be evaluated corneometrically and elastometrically, on the skin level. The chemical extraction and analysis of *Anethum graveolens* essential oil was performed using CG – MS, and skin tests were done with corneometer and elastometer Courage – Khazaka Electronic. Volunteers had criteria for inclusion in the study group and a protocol of application and testing. Results. Thus, 13 major components were identified in the *Anethum graveolens* essential oil: Trans-beta-ocimene: 0.138, Lavandulol: 0.065, Alpha-phellandrene: 1.499, p-cymene: 0.211, D-limonene: 73.546, α-Ethylacrylonitrile: 0.049, 1-Butene: 0.007, Norbornane: 1.067, Estragole: 0.121, Piridine: 0.064, D-carvone: 17.829, 1H-Imidazole: 0.014, Anethole: 4.981. Clinical skin testing demonstrated a reversible increase in moisture and elasticity skin parameters at the product application moment. Subsequently, at 30 days of testing, there was only a persistent increase in skin elasticity. Beyond the beneficial effects in aromatherapy of this common plant, additionally estrogenic beneficial properties are reported in literature. By comparing the chemical compounds evaluated in this study with our previous studies on the essential oil of *Lavandula angustifolia*, we can note some common substances, for which we already reported a depigmenting effect of the skin (inhibition of tyrosinase). Observing the chemical components of the *Anethum graveolens* essential oil we consider that it can be further tested, in order to identify other cutaneus benefits. Our preliminary skin tests demonstated that: (1) the product is fast but reversible moisturizing for skin due to the excipients, and (2) the finished product is a lasting elasticity inducer, via the active compound.

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Keywords: *Anethum graveolens*, composition, antiaging, skin.

OBPC P-17

MANNICH-TYPE APPROACH TO CHIRAL AMINO-QUINOLINOLS - SYNTHESIS AND APPLICATION

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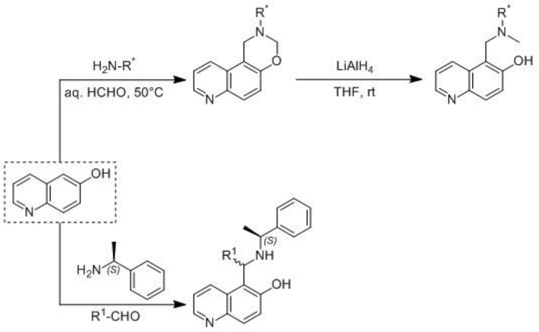
The Mannich reaction is one of the most frequently applied multicomponent reactions in organic chemistry. In the original form of the reaction, the Mannich product is formed through the reaction of a C-H acid, formaldehyde and a secondary amine.

A special alteration is the three-component modified Mannich reaction in which formaldehyde is replaced by an aromatic aldehyde, the secondary amine by different N sources, and the C-H acid by an electron-rich aromatic compound such as 1- or 2-naphthol, quinolinol or isoquinolinol, is known as Betti-condensation.[1] The use of non-racemic amines in this type of condensation has opened a new area of applications of the chiral nonracemic products formed as catalysts in enantioselective transformations.[2]

We are presenting herein the syntesis of chiral 1,3-aminoquinolinols using different aldehydes, 6-hydroxyquinoline, as 2-naphthol analogue and chiral amines.



The stereoselectivity of the condensation reaction has been studied and the individual diastereoisomers have been isolated in pure form. The configurations of the newly formed stereogenic centres were determined through application of advanced NMR experiments and X-ray crystallography.

The aminoquinolinols obtained as pure diastereoisomers have been applied as catalysta in the enantioselective addition of Et2Zn to aldehydes. In most cases exellent yields of isolated secondary alcohols and high degree of enantioselectivity were achieved.

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Acknowledgements: Bulgarian National Science Fund (Projects UNA-17/2005, DRNF-02-13/2009; DRNF-02/1/2009). The support of project H2020-MSCA-RISE-2015 No. 691247 (EXANDAS) is greatly acknowledged.

Keywords: aminoquinolinols, mannich reaction, enantioselectivity.

OBPC P-18

PREPARATION OF CHIRAL NONRACEMIC AMINOBENZYLNAPHTHOLS BY BETTI- CONDENSATION AND CATALYTIC APPLICATIONS

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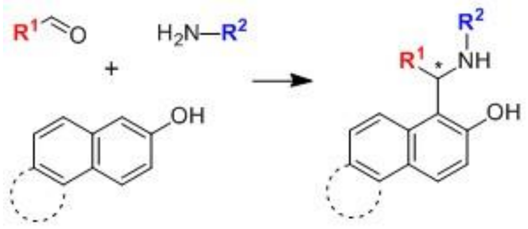
The three component condensation of Betti-type offers very convenient method for the synthesis of aminobenzylnaphthols by using readily available 2-naphthol, aldehydes and amines. By using of chiral amines, chiral nonracemic aminobenzylnaphthols could be synthesized with high diastereoselectivity. Thus it is possible to prepare structurally diverse aminoalcohols possessing excellent properties to be used as ligands for enantioselective addition of diethylzinc to aldehydes.

We are presenting the synthesis of chiral 1,3-aminonaphthols realizing the condensation with different aromatic aldehydes, substituted 2-naphthols and chiral amines. In all cases solvent free procedure was applied and the desired products were isolated in acceptable yields. The diastereoselectivities observed were excellent and the individual diastereoisomers could be isolated in pure form by means of column chromatography.



The configurations of the newly formed stereogenic centres were determined through application of advanced NMR experiments and X-ray crystallography. The new aminobenzylnaphthols were applied as chiral ligands for enantioselective addition of diethylzinc to aldehydes with high degree of enantioselectivity (up to 97% ee).

Acknowledgements: This work was promoted by the Support Program for career development of young scientists, BAS (Project DFNP-149/2016); Bulgarian National Science Fund (Projects UNA-17/2005, DRNF-02/1/2009).

Keywords: Betti condensation, aminobenzylnaphthol, NMR spectroscopy, X-ray crystallography.

OBPC P-19

GREEN SYNTHESIS OF SILVER NANOPARTICLES USING *Basil* EXTRACTS AND EVALUATION OF GENOTOXIC ACTIVITY

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The extracts of different types of basil (Sweet Basil, Greek Basil, Purple Ruffles) were used for the synthesis of silver nanoparticles. The method of nanoparticles with plants extracts is already well known [1]. From each species extracts of leaves, stalk and roots were collected to be used in the synthesis reaction. The formation of silver nanoparticles in the reaction vessel (AgNPs), was monitored by ultraviolet-visible spectroscopy (UV-Vis) [2]. The indication for the synthesized nanoparticles was an absorption peak which appeared at 430 nm in the UV spectrum. Also the genotoxic effect of extracts was determined and obtained results showed that some extracts (leaves of Purple Ruffles and stalk of Greek Basil) have higher genotoxic effect.

Acknowledgements: Ministry for Education, Science and Technology of the Republic of Kosovo.

Keywords: sweet basil, Greek basil, purple ruffles, extracts, silver nanoparticles, UV-VIS spectroscopy, genotoxicity.

OBPC P-20

GREEN SYNTHESIS OF SILVER NANOPARTICLES USING *Ginger* AND *Aloe vera* EXTRACTS AND EVALUATION OF GENOTOXIC ACTIVITY

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The synthesis of nanoparticles using plants extracts is a cheap and environmentally compatible method, since it avoids the use of synthetic chemicals [1]. The extracts of medical plants Aloe Vera and Ginger were used for the synthesis of silver nanoparticles. In the synthesis procedure, the extract of Aloe Vera leaves were used, while from Ginger leaves and roots were taken as extract source. The reaction of the synthesis of silver nanoparticles (AgNPs), was monitored by ultraviolet-visible spectroscopy (UV-Vis) [2]. A well-defined relatively broad peak at 430 nm appeared as a signal of the presence of silver nanoparticles in the system. Also the genotoxic effect of extracts was determined and obtained results showed that some extracts (leaves of Aloe Vera and roots of Ginger) have the same genotoxic effect, while the leaves from fresh ginger have higher genotoxic effect.

Acknowledgements: Ministry for Education, Science and Technology of the Republic of Kosovo.

Keywords: Ginger, Aloe Vera, extracts, silver Nanoparticles, UV-VIS spectroscopy, genotoxicity.

OBPC P-21

GLUCOSINOLATE PROFILING OF *Bunias erucago* L., *Matthiola incana* (L.) R. Br. AND *Lepidium sativum* L. (Brassicaceae)

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Glucosinolates (GLs) are secondary metabolites present in 16 botanical families of the Capparales Order, among which the most important is Brassicaceae family, which includes well-known plants of everyday nutrition such as cabbage, broccoli, cauliflower, broomsticks, radish, beets and others. Chemically these are *β*-thioglucoside-*N*-hydroxysulfates with a variable side chain mostly aliphatic, and arylaliphatic ones [1].

In this study, GLs were characterized by GC-MS analysis of their breakdown products in various parts of *Bunias erucago* L., *Matthiola incana* (L.) R. Br. and *Lepidium sativum* L., and quantified according to the ISO 9167-1 official method based on the HPLC analysis of desulfoglucosinolates [2]. Three GLs, namely glucoerucin (GER), gluconapin (GNA) and glucotropaeolin (GTL) were identified in *B. erucago*, one GL, glucoraphenin (GRE) in *M. inacana*, and one, GTL, in *L. sativum*. The total GL contents in *B. erucago* were 17.0, 11.8, and 9.0 μmol/g dry weight in root, flower, and leaf and stem, respectively, with GNA as the major GL detected in all parts, followed by GER and GTL. *M. incana* total GL content was represented by GRE having 11.3, 2.8, 2.4, 2.1, 0.8 μmol/g dry weight in seed, flower, siliquae, stem, and leaf, respectively, while GTL represented the total content of *L. sativum* seed having 18.7 μmol/g dry weight.

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Acknowledgements: The research was funded by Croatian Science Foundation project BioSMe (IP-2016-06-1316).

Keywords: glucosinolates, isothiocyanates, GC-MS, HPLC.

OBPC P-22

SYNTHESIS OF BENZENE AND FEROCENE SULFONAMIDES WITH POTENTIAL ANTIMYCOBACTERIAL ACTIVITY

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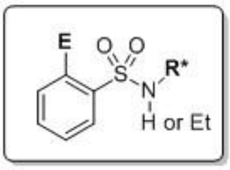
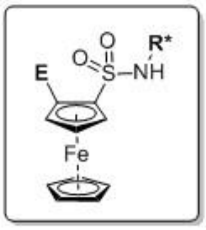
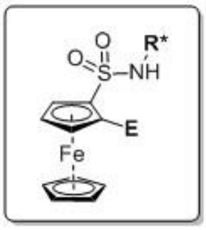
The biological activity of sulfonamides was first noted in 1932, when Domagk observed the antimicrobial effect of Prontosil® on Streptococcus infections in mice. Sulfa drugs are notably used to treat a wide range of pathogenic microorganisms, such as Mycobacterium tuberculosis [1], Escherichia coli, Salmonella, Enterobacter species [2], Candida albicans, Aspergillus fumigatus, Aspergillus niger [3] etc.

Due to the stability of the ferrocenyl group in aqueous and aerobic media and its favorable electrochemical properties, ferrocene and its derivatives have been recognized as suitable molecules for biological applications [4]. Surprisingly, there is no data in the literature concerning the biological activity of ferrocene sulfonamides. Recently, we have investigated several (+)-camphor derivatives bearing ferrocenylmethylidene and sulfonamide moieties that have shown promising cytotoxic and cytostatic activities against a large set of cancer and normal human cell lines [5].

Herein is reported the synthesis of new chiral benzene and ferrocene sulfonamides with potential biological activity. Selected compounds were evaluated for *in vitro* antibacterial activity against *Mycobacterium tuberculosis* $H_{37}Rv$ and have shown excellent antimycobacterial activity.







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Acknowledgements: The support of project H2020-MSCA-RISE-2015 No. 691247 (EXANDAS) is greatly acknowledged.

Keywords: Chiral sulfonamides, antimycobacterial activity.

OBPC P-23

CHEMICAL COMPOSITION AND ANTIMICROBIAL ACTIVITY OF SOLVENT EXTRACTS OF *Artemisia scoparia* Waldst. et Kit.

Jovana Ickovski, Katarina Stepić, Aleksandra Đorđević, Ivan Palić, Goran M. Petrović, Gordana Stojanović
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Not presented.

OBPC P-24

CHEMICAL COMPOSITION OF *Satureja kitaibelii* Wierzb. ex Heuff. ESSENTIAL OILS FROM SERBIA DURING DIFFERENT STAGES OF VEGETATIVE DEVELOPMENT

Ivan Palić, Jovana Ickovski, Aleksandra Đorđević, Violeta Mitić, Goran M. Petrović,
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Not presented.

OBPC P-25

NEW ORGANIC LUMINOPHORES – PREPARATION, STRUCTURE AND FLUORESCENCE PROPERTIES

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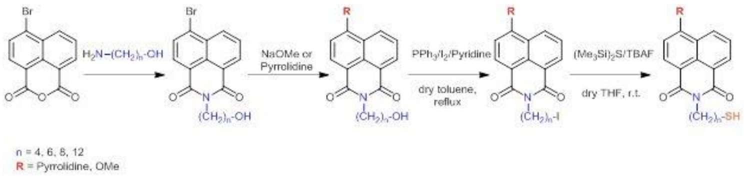
The development of functional 1,8-naphthalimide derivatives as DNA targeting, anticancer and cellular imaging agents is a fast growing area and has resulted in several such derivatives entering into clinical trials. [1] In a previous study *N*-substituted 1,8-naphthalimides especially designed for fluorescent labeling of gold nanoparticles has been synthesized. [2] They contain a long methylene chain at the imide *N*-atom and a terminal SH group, which enables its chemical binding to gold nanostructures. The longest wavelength absorption maximum of the tiols in chloroform is at about 370 nm, the fluorescent maximum is at about 430 nm and the fluorescent quantum yield is up to 0.95.



A series of new fluorescent naphthalimide thiols containing four, six and twelve membered unbranched aliphatic chains respectively were synthesized in four steps. All 1,8-naphthalimides (including intermediates) were isolated in pure form (column chromatography) and characterized by NMR, melting points and masspectrometry. The newly synthesized fluorophores are suitable for modification of AuNPs.

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OBPC P-26

BORANE-MEDIATED ASYMMETRIC REDUCTION OF KETONES BY STERICALLY HINDERED AMINODIOLS AS CHIRAL LIGANDS

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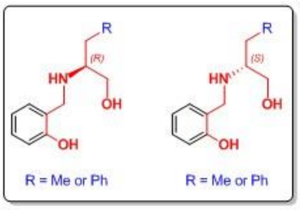
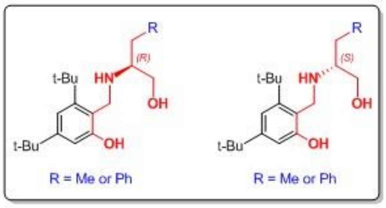
Borane-mediated asymmetric reduction of ketones has emerged as a standard method for generating enantiomerically pure secondary alcohols as significantly important intermediates or chiral building blocks for the synthesis of biologically active structures. In the original studies of *Itsuno* and *Corey* this reaction is catalyzed by monocyclic chiral oxazaborolidines either formed *in situ* or prepared separately from a variety of aminoalcohols [1]. Subsequent to the discovery of the high enantioselectivity demonstrated by the proline-derived *CBS* catalyst in the reduction of ketones with BH_3, many other fused bicyclic oxazaborolidines have been reported by other research groups [2]. Commonly, bicyclic oxazaborolidines, obtained from tridentate ligands containing one nitrogen and two oxygen atoms, can increase the differentiation of the enantiotopic faces of the carbonyl compound and the affinity of the ketone binding to boron, because of the rigidity of the bicyclic skeleton and to the increased Lewis acidity of the coordinated boron atom.

Herein we present a synthetic approach for the preparation of a small series of sterically hindered chiral aminodiols incorporating 2-aminobutanol or 2-phenylglycinol moiety. Surprisingly, the data concerning the use of these two aminoalcohols in asymmertic reductions is scarce. Only the (*R*)-enantiomer of 2-phenylglycinol is reported as chiral ligand for enantioselective borane reduction - a key step in the synthesis of (*R*,*R*)-formoterol [3]. Recently we have found that both (*R*)- and (*S*)-enantiomers of 2-aminobutanol exhibit relatively high enantioselectivity (71 (*R*) and 83 (*S*) *ee*, respectively) and have not been previously applied as chiral ligands in asymmetric reductions. The novel enantiopure compounds have been obtained using simple synthetic routes. They were applied as chiral tridentate ligands in enantioselective borane reduction ($BH_3{\bullet}SMe_2$) of α-chloroacetophenone.





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Keywords: asymmertic borane reduction; chiral ligands; aminoalcohols.

OBPC P-27

TOTAL FLAVONOID CONTENTS IN THE EXTRACTS OF BLACK LOCUST FLOWERS

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Black locust flower (*Robinia pseudoacacia* flos) is a main source of various bioactive compounds with expressed pharmacological activity [1,2]. The aim of this paper was to determine the total flavonoid contents of black locust extracts using the spectrophotometric method with aluminum chloride. The flavonoid content was expressed as milligrams of rutin equivalent per 100 g dry plant material (mg_{RE}/100 g d.p.m.). In order to investigate the impact of solvents polarity on the yield of flavonoids, the five different solvents (water, methanol, ethanol and their combinations) were analyzed. The extractions were performed under reflux at the extraction temperature of 60 °C for 35 min. The lowest total flavonoid content was 1168 mg_{RE}/100 g d.p.m. in the extract obtained using 96% (v/v) ethanol, while this content (1937 mg_{RE}/100 g d.p.m.) was the highest in the extract obtained using 50% (v/v) methanol. The total flavonoid contents of 1573 and 1621 mg_{RE}/100 g d.p.m. were almost the same in the extracts obtained using ethanol (50%, v/v) or methanol solvents, respectively. The determined content of flavonoids in the aqueous solution was 1300 mg_{RE}/100 g d.p.m. The results indicated that the extracts of black locust flowers had a high content of flavonoids. The further study will be focused on the analysis of correlation between antioxidant activity and total flavonoid content.

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Acknowledgements: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia under the project TR-34012. Ivana Boskov is a scholar of Ministry of Education, Science and Technological Development of the Republic of Serbia.

Keywords: total flavonoids, extraction, spectrophotometry, reflux.

OBPC P-28

EFFECT OF EXTRACTION SOLVENTS ON THE ANTIOXIDANT ACTIVITY OF BLACK LOCUST FLOWERS

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Black locust flower (*Robinia pseudoacacia* flos) is a source of vitamin C, phenolic compounds, resins, tannins, essential oils, monoterpenes, diterpenes, triterpenes, and small amount of poisonous robinin that completely disappears after thermal treatment and drying [1,2]. In folk medicine, it is used for alleviating the colds and coughs, cramps in the stomach, rheumatic pains, migraine, fever, and skin diseases [3]. The impact of extraction solvents on the antioxidant activity of the extracts of black locust flowers was investigated under reflux. The plant material was treated with water, absolute ethanol, methanol, 50% (v/v) ethanol or 50% (v/v) methanol at the extraction temperature of 60 °C for 35 min. The antioxidant activity of these extracts was determined using DPPH assay, and estimated based on the half maximal inhibitory concentration (IC_{50}). The lowest IC_{50} value (0.47 mg cm^{-3}) had the aqueous extract, while the highest IC_{50} value (1.66 mg cm^{-3}) had the methanol extract. These values were found to be 0.5 and 0.7 mg cm^{-3} for the extracts obtained using 50% (v/v) ethanol or 50% (v/v) methanol, respectively. Since the aqueous extract had the lowest IC_{50} value in compared with other extracts, it can be concluded that the extract of black locust flowers possessed the highest antioxidant activity. The obtained results have shown that the better antioxidant activity was obtained using the aqueous organic solvents in compared with the respective absolute organic solvents. This is probably the result of extraction of the high content of polar bioactive compounds with expressed the antioxidant activity. Due to the application of the green solvent (water), the extract can be used as the ingredient in the food or pharmaceutical industries. The further experiments related to the biological activities of these five extracts are currently in progress.

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Acknowledgements: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia under the project TR-34012. Ivana Boskov is a scholar of Ministry of Education, Science and Technological Development of the Republic of Serbia.

Keywords: extraction, antioxidant activity, solvents, reflux, DPPH assay.

OBPC P-29

QSAR MODELS FOR ASSESSMENT OF THE POTENTIAL OF AZAINDOLE ANALOGS AS HIV-1 ATTACHMENT INHIBITORS

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Human immunodeficiency virus – 1 (HIV-1) glycoprotein 120 (gp120) is one of the key targets for Acquired immunodeficiency syndrome (AIDS). A large number of inhibitors are being designed for this target in order to find safe and effective drugs. In the present study, we have developed QSAR models for HIV-1 attachment inhibitors based on data for 128 azaindole analogs using suitable molecular descriptors calculated by Dragon software. Chemometrics methods including multiple linear regression (MLR), artificial neural network (ANN) and support vector machine (SVM) were used to set up QSAR models in order to explain the structural requirements of HIV-1 gp120 inhibitory activity. The performance and predictive capability of the SVM method were investigated and compared with other techniques. The contribution of each descriptor to the structure-activity relationships was evaluated. The correlation coefficients for both the training set and test set reveal that the SVM model is slightly superior to the ANN one. The results obtained indicate that both models can be successfully used to predict the anti-HIV-1 activity of the studied compounds. These computational studies have potential application in the prediction of biological activity for the newly synthesized compounds.

Acknowledgements: The study was partly funded by the joint project "Molecular Modelling of HIV Inhibitors" of the Francophonie University Association (AUF) and the Bulgarian National Science Fund.

Keywords: Quantitative Structure-Activity Relationship (QSAR), HIV-1, gp120, MLR, ANN, SVM.

OBPC P-30

EFFECTS OF PARTICLE SIZE AND SOLID TO LIQUID PHASE RATIO ON THE YIELD AND COMPOSITION OF THE ESSENTIAL OIL FROM THE WILD OREGANO

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Essential oils are a mixture of volatile lipophilic compounds that are mostly obtained from leaves, flowers, branches, wood pulp or bark tissue of the aromatic and medical plants. A great number of plant varieties are valued according to essential oil content. It is known that the wild oregano essential oil shows remarkable biological properties. Various studies have reported that the antimicrobial, antimycotic, antioxidant, anti-inflammatory and insecticidal effect of plant products, is *mainly* attributed to *phenolic compounds* e.g. carvacrol [1]. Hydrodistillation is a traditional method normally used to isolation essential oils from plants. It provides a high quality of essential oil and also represents a relatively simple, safe and environmentally friendly process. [2].

The objective of this study was to investigate the effects of the particle size and solid-to-liquid ratio on the yield, as well as, the qualitative and quantitative composition of the obtained essential oil from wild oregano (*Oreganum onites* L.). The samples of the wild oregano with 0.25 mm and 0.5 mm particle size at solid-to-liquid ratio of 1:5 *w/v*, 1:10 *w/v* and 1:15 *w/v* were distillated for 180 min using an Unger-type apparatus. The collected essential oils were dried over anhydrous sodium sulfate and stored at 4°C for further analysis.

The GC-MS analyses were performed in an Agilent 5973N mass selective detector coupled to an Agilent 6890 gas chromatograph (Palo Alto, CA), equipped with an HP-Innowax capillary column (60 m x 0.25 mm x 0.25 µm), operating in electronic ionization mode at 70eV. Helium was the carrier gas (1.0 mL min^{-1}). The injector temperature was kept at 250 ºC and the oven temperature program was from 60º for 10 min to 220 ºC at a rate of 4 ºC min^{-1} and finally holding at 240 °C for 30 min. Pure oils were injected in split mode (60:1). The components *were identified* by *comparison of* their mass *spectra* (MS) and retention indices (RI) with those reported in the literatureand also to the Wiley Registry of Mass Spectral Data, 8th Edition (Wiley Interscience, New York).

The influence of the wild oregano particle size on the essential oil yield is significant. The quantity of essential oil increased by increasing the particle size from 0.25 mm to 0.5mm. The solid-to-liquid ratio had the insignificant effect on the yield of essential oils obtained from *Origanum onites* L. The *highest quantity* of the essential oils (1.31% w/w) was obtained with the hydrodistillation of the wild oregano with 0.5 mm particle size at 1:15 w/v solid-to-liquid ratio. A total of 24 compounds were identified in the *Origanum onites* essential oils with the GC-MS analysis. The major compounds were: carvacrol (61.95%-80.61%), linalol (3.71%-7.41%), thymol (2.37%-5.15%), terpinen-4-ol (2.21%-5.38), borneol (2.22%-4.70%) and β-bisabolene (1.15%-2.74%).

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Keywords: essential oil, particle size, solid to liquid phase ratio, yield, carvacrol.

OBPC P-31

EFFECT OF SOLVENT COMPOSITION ON EXTRACTION OF TOTAL FLAVONOIDS FROM UNFERMENTED TOBACCO

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It is *estimated* that *5,200 compounds have been identified in tobacco.* Among them, flavonoids are widely distributed secondary metabolites in tobacco. Flavonoids possess anti-oxidative, anti-inflammatory, anti-mutagenic and anti-carcinogenic properties. They are considered as health promoting and disease preventing supplements. In comparison to conventional methods such as maceration, percolation or *Soxhlet* extraction, the ultrasound-assistant extraction as modern technique offers a high yield of analyzed compounds in a short time as well as simple manipulation, lower energy input and high reproducibility.

In this study, the unfermented leaves of the oriental tobacco type Basmak, the varieties MK-1 and MB-2 were extracted by using ultrasound-assisted method and acetone, methanol and ethanol as solvent in concentration of 50 *v/v*%, 75 *v/v*% and 100 *v/v*%. The extraction conditions were 0.25 mm material particle size, 1:50 solid to liquid phase ratio, 40 ºC temperature, 30 min time and 300 W ultrasound power. The efficiency of ultrasound-assisted method was compared to *Soxhlet* extraction performed at 1:20 solid to liquid phase ratio with 80 *v/v*% methanol in duration of 8h.The total flavonoids content was determined by the aluminum chloride colorimetric method described by Chang *et al.* [1] with modifications. Flavonoid content of the extracts was calculated from the regression equation of calibration curve ($y = 0.0031x+0.0159$; $r^2 = 0.9997$, y - value for absorbance of the sample, x - sample concentration, r^2 - correlation coefficient) and expressed as mg of quercetin equivalent per gram of dry plant material (mg_{QE}/g DW). UV absorption spectra were measured between 300 nm and 500 nm using a 10-mm cell and a double beam spectrophotometer.

With increasing the *polarity* of *solvent, the quantity* of obtained extract from the leaves of the oriental tobacco type Basmak increased. The highest yield of extract was obtained with 100 *v/v*% methanol, the variety MK-1 (31.30 g/100 g DW) and the variety MB-2 (30.22 g/100 g DW). The *total flavonoid content* of *different* solvent extracts decreased in the following order: 100 *v/v*% acetone > 75 *v/v*% aqueous acetone >100 *v/v*% ethanol > 75 *v/v*% aqueous methanol > 50 *v/v*% aqueous acetone > 75 *v/v*% aqueous ethanol > 50 *v/v*% aqueous ethanol > 100 *v/v*% methanol and 50 *v/v*% aqueous methanol. The highest total flavonoids content was determined in the *extracts* from a *variety* of MK-1 and MB-2 obtained with 100% acetone as it follows 118.11 mg mg_{QE}/g DW for the variety MK-1 and 99.57 mg mg_{QE}/g DW for MB-2. The *quantity* of obtained extract and the total flavonoid content obtained by applying *Soxhlet* method were 29.10 g/100 g DW and 90.03 mg_{QE}/g DW for the variety MK-1 and 28.61 g/100 g DW and 82.10 mg_{QE}/g DW for the variety MB-2. These results indicate that the extracts of the unfermented tobacco obtained with the appropriate solvent can be used as a source for isolation of the flavonoids for food and pharmaceutical purposes.

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Keywords: total flavonoids, tobacco extracts, spectrophotometry, Soxhlet extraction, ultrasound-assisted extraction.

OBPC P-32

BIOLOGICALLY ACTIVE CELLULOSIC MATERIAL WITH THE BOUND CEFAZOLIN

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Biologically active fibers as drug carriers have improved characteristics in comparison with conventional medical therapies. Cellulose as a hydrophilic and biocompatible, nontoxic and eco-friendly material, makes a good polymer matrix for obtaining biologically active fibers.

Biologically active fibers as drug carriers have improved characteristics in comparison with conventional medical therapies Cellulose as a hydrophilic and biocompatible, nontoxic and eco-friendly material, makes a good polymer matrix for obtaining biologically active fibers.

In this paper the oxidized cellulose with different carboxyl group content is obtained by selective oxidation and used for chemical bonding of antibiotic cefazolin in order to obtain the biologically active material.

The bonding was performed in antibiotic water solution concentration of c=3,4·10^{-3} mol/L at temperature 20±1 °C, while desorption was performed in physiological solution. The amounts of bonded and released antibiotic were determined spectrophotometrically in UV range. Maximum amount of the bound drug (0,0337 mmol/g) was obtained during the sorption on the oxidized bandage with 2,276 mmol/g COOH and the maximum amount of the released drug was 0,0091 mmol/g. Antimicrobial activity of the samples with bound cefazolin was tested *in vitro* against *Staphylococcus aureus*, *Bacillus subtilis and Escherichia coli* by agar diffusion test.

The paper studies the influence of cefazolin chemical structure and duration of sorption on the amount of the bound drug. It was determined that the drug bonding was primarily achieved by hydrophobic interactions of the drug functional groups with the oxidised cellulose bandage.

Acknowledgements: Ministry of Science and Technology of the Republic of Srpska.

Keywords: modified cellulose, cefazolin, biologically active cellulosic material.

OBPC P-33

DETERMINATION OF TOTAL PHENOLIC, FLAVONOID, ANTHOCYANIN CONTENTS AND ANTIOXIDATIVE ACTIVITY OF ETHANOLIC EXTRACTS OF BLACKTHORN FRUITS (*Prunus spinosa* L) FROM BOSNIA AND HERZEGOVINA BY SPECTROPHOMETRIC AND CYCLIC VOLTAMMETRY METHODS

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Prunus spinosa L. also known as blackthorn or sloe is a plant from the *Rosaceae* family. It grows wild in various regions in Bosnia and Herzegovina. Blackthorn is commonly used in the food industry and phytotherapy for the treatment of many diseases related to various forms of a cough; it is a mild laxative, diuretic, spasmolytic and anti-inflammatory agent. It has an antiseptic effect because of the presence of tannins and shows activity against inflammation of the mucosal layer of the digestive system. Blackthorn is particularly rich in antioxidants, such as vitamins C and E, carotenoids and flavonoids, routine and quercetin- which are considered to be one of the strongest natural antioxidants. Total phenolic, flavonoid, anthocyanin contents and antioxidative activity of ethanol extracts of fruits from *Prunus spinosa* were quantified by spectrophotometric methods. Cyclic voltammetry and "radical scavenging" method with DPPH radical were used to determine the antioxidant activity. Three samples from different areas from Bosnia and Herzegovina (Vareš, Trnovo, Borije) were investigated. Ethanolic extracts were obtained by Soxhlet extraction and Ultrasound assisted maceration. The content of total phenol compounds varies from 1,72 to 3,21 mg GAE/g of fresh fruit. The differences in total phenol compounds content depend on used extraction methods for the samples as well as from the different areas from which the samples were collected. Total flavonoids content ranges from 1,01 to 1,86 mg QE/g of fresh fruits. The content of anthocyanins lies between 0,20 to 1,95 mg cyanidin 3-glucoside/g of fresh sample in ethanol extract. All explored extracts exhibited strong scavenging activity against DPPH radicals, which ranges from 31,86 to 78,96%. At the same time, cyclic voltammetry was performed on three extract samples. Cyclic voltammograms of all blackthorn fruit ethanol extracts showed an oxidation wave at the potential of 0,52 V, which is derived from quercetin, a polyphenolic flavonoid present in blackthorn fruits. This value correspondes with literature velue for quercetin.

Blackthorn fruit extract exhibits a phenolic content and a high antioxidant activity and can be used as an antioxidant in food and pharmaceutical industries. To the best of our knowledge, determination of antioxidant activity of blackthorn fruit ethanolic extracts by the cyclic voltammetry was attempted for the first time in this study. The differences that exist in the measurement results for different ethanol extracts are due to different localities from which fruits originate, as well as different ways of processing.

Keywords: blackthorn fruit, ethanolic extract, flavonoids, antioxidative, Cyclic voltammetry.

OBPC P-34

PAHs CONTAMINATION IN ELBASANI METALLURGICAL COMPLEX, ALBANIA

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Numerous sources of PAHs have been shown to alter the composition of PAHs and in some cases increase the fractions of carcinogenic components. Therefore, this study was carried out to determine the levels of seven potentially carcinogenic PAHs (BaP, BaA, Chry, BbF, BkF, IND and DahA) in twenty-one soil samples collected in March 2017 throughout the Metallurgical Complex area, in Elbasan, Albania. The industrial units cover a wide range of activities, giving rise to the emission of a wide variety of organic and inorganic pollutants. Surface soil samples were analyzed using an UAE/GC-MS method. The content of Σ7 PAHs ranged from 58.7-139,819 µg kg^{-1}, with a median value of 398 µg kg^{-1}. The highest concentration of the total carcinogenic PAHs was found in Station I7 (coke plant) with a value of 139,819 µg kg^{-1}. The concentrations of the carcinogenic PAHs in soils follow this decreasing trend: BbF > Chry > IND > BaA > BaP > BkF > DahA. The most carcinogenic PAH (BaP) was found with a median value of 52.87 µg kg^{-1}. Moreover, the values of toxic equivalent concentrations based on BaP$_{eq}$ ranged from 14.39-32,970 µg kg^{-1}. The highest TEQ$_{carc}$ value was found in station I7 due to the very high PAHs concentrations. Levels of BaP in some stations were found higher than the limit value of the Canadian soil quality guideline. The analytical results indicated that the activity of the metallurgical complex was the major sources of PAHs in Elbasani area.

Keywords: industrial activity, carcinogenic PAHs, benzo(a)pyrene, gas chromatograph.

OBPC P-35

IMPLEMENTATION OF ICH Q3D GUIDELINE IN THE PHARMACEUTICAL INDUSTRY – WHAT SHOULD WE KNOW ABOUT THE HEAVY METALS IN THE COMMERCIAL DRUGS

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International Conference on Harmonization (ICH), Q3D Guideline for Elemental Impurities have introduced the pharmaceutical industry with new challenge- replacing the wet chemical limit test “heavy metals” with new analytical technologies - inductively coupled plasma (ICP)- based techniques along with new limits and approaches for determination of elemental impurities. A risk assessment that is accurately effected and documented will be used to define the control strategy for testing of elemental impurities in the finished drug product alongside with specifically determined limits in reference with the daily intake of the drug. While the Q3D guideline is ultimately intended to focus on final drug product quality, the actual risk assessment will touch all starting materials and steps of the manufacture of a drug product. The outcome of the risk assessment will determine the need for elemental impurity testing, is testing should be reduced or even eliminated if there is adequate control. If the risk assessment declares that all elemental impurities are below 30% PDE as control threshold additional testing may not be necessary. Although the main challenge is implementation of the guideline requirements in cases where additional testing is considered necessary. The lack of available literature and information regarding sample preparation, digestion of the samples and instrumental sets of parameters when is complex drug product introduced is main and daring problem.

This paper summarizes a recent survey of elemental impurity testing in common pharmaceutical drug products as well as screening for elements in industrial and drinking water using microwave digestion technique as sample preparation step using common mixtures of high purity metal- basis acids. The analyses were carried out on ICP-OES instrument using previously developed and validated methods.

Keywords: ICH (Q3D), Elemental impurities, ICP-OES.

OBPC P-36

SYNTHESIS OF MONOCARBONYL CURCUMIN ANALOGS AND UV-VIS STUDIES OF THEIR INTERACTIONS WITH THIOLS

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In order to improve the bioavailabilty of curcumin, studies have been undertaken to prepare the so-called monocarbonyl curcumin analogs and also to assess their biological activity. It has been established that these analogs contain potentially electrophilic α,β-unsaturated carbonyl moiety (Michael acceptor activity). Several key biological processes are connected/controlled with thiol alkylation (glutathione, cysteine, cysteine peptide residues). The most likely reaction is the thia-Michael addition between the α,β-unsaturated acceptor and the corresponding thiol. It would be convenient to be able to vary the electrophilicity and redox properties of the Michael acceptor by introduction of various substituents. Several monocarbonyl curcumin analogues based on the 2,6-bisarylidenecyclohexanone scaffold offer such an opportunity. In this study they were prepared by aldol condensation reaction between cyclohexanone and the corresponding monosubstituted benzaldehydes. Special care was undertaken to purify these solid analoges via recrystallization from the appropriate solvent.

UV-Vis spectra were recorded of these synthesized dervatives and then a proper system for evaluation of their reaction with certain thiols were investigated (optimization of pH, solvent(s), mixing procedure, avoiding thiol oxidation. The key of this study was finding appropriate thiol (cysteine, glutathione (GSH), cysteamine, 2-mercaptoethanol etc.) and concentration for assessing its interaction with 2,6-bisarylidenecyclohexanone analogs.

Keywords: synthesis; monocarbonyl cucrcumin derivatives; thiols; Michael addition.

OBPC P-37

SYNTHESIS AND COMPARATIVE STRUCTURAL STUDY OF (2*E*,6*E*)-4-*TERT*-BUTYL-2,6-BIS(2-FURYLMETHYLENE)CYCLOHEXANONE AND (2*E*,6*E*)-2,6-BIS(2-FURYLMETHYLENE)CYCLOHEXANONE

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The aim of this study was to synthesize and purify two structurally related derivatives - (2*E*,6*E*)-4-*tert*-butyl-2,6-bis(2-furylmethylene)cyclohexanone and (2*E*,6*E*)-2,6-bis(2-furylmethylene)-cyclohexanone and then carry out structural studies using infra red spectroscopy and X-ray powder diffractometry (XRPD). The title compounds were prepared in excellent yields (80-85%) using crossed aldol reaction between cyclohexanone or 4-*tert*-butylcyclohexanone and furfural. They were purified from appropriate solvents (methanol or ethyl acetate) and their melting points and spectroscopic properties matched the ones from the literature. From the IR spectroscopic studies (KBr pellet and FT-IR-ATR) it was established that the characteristic carbonyl (C=O) stretching frequency for (2*E*,6*E*)-2,6-bis(2-furylmethylene)-cyclohexanone was at 1645 cm^{-1}, whereas for the 4-*tert*-butyl-2,6-bis(2-furylmethylene)cyclohexanone it was at 1654 cm^{-1}. This difference of ~10 cm^{-1} has been observed in other 2,6-bisbenzylidenecyclohexanone derivatives (cyclohexanone vs. 4-*tert*-butylcyclohexanone core). Further investigation to obtain structural data from was done using XRPD spectra and also literature data from X-ray single crystal structure of (2*E*,6*E*)-2,6-bis(2-furylmethylene)cyclohexanone. Computational methods were used to further investigate the structural features of these two derivatives with focus on the conformational effects versus solid state packing effects. Similar compounds have been used to create organic polymers and NLO materials that may have application in the future. The information obtained from this study can also be extended and continued on other 2,6-bisbenzylidenecyclohexanone derivatives, which is planned for future work.

Keywords: synthesis, structural studies, infrared spectroscopy, XRPD.

OBPC P-38

SYNTHESIS, PURIFICATION AND COMPUTATIONAL STUDIES OF BIOACTIVE SYMMETRICAL MONOCARBONYL ANALOGS OF CURCUMIN BASED ON THE 2,6-BISARYLIDENECYCLOHEXANONE CORE

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The bioavailability of curcumin can be improved by replacing the β-diketo moiety with single carbonyl group. These so-called monocarbonyl analogs of curcumin (MAC) have exhibited various biological activity and it has been established that the pharmacophore is 1,5-diaryl-3-oxo-1,4-pentadienyl bearing two active arylidene groups conjugated with a keto group. In this study we have chosen the symmetrical 2,6-bisarylidenecyclohexanones due to synthetic accessibility, relative structural “rigidity”, simplified computations and established biological activity. The α,β-unsaturated keto group is known thia-Michael acceptor and reacts preferentially with biologically relevant thiols and not with amino or hydroxyl groups. These systems should exhibit no mutagenic effects which are exhibited by certain alkylating therapeutic agents. Also these bifunctional Michael acceptors can undergo successive attacks of cellular thiols. Many of these derivatives have been prepared in high yields by straightforward crossed aldol condensation between cyclohexanone and the corresponding substituted benzaldehyde under basic conditions. The MACs can be obtained in high purity usually by recrystallization from appropriate solvent (ethanol, methanol, methanol/CH_2Cl_2 and ethyl acetate).

Two MACs have been tested *in vivo* ((2*E*,6*E*)-2,6-bis[2-(trifluoromethyl)-benzylidene]cyclohexanone and (2*E*,6*E*)-2,6-bis(2-bromobenzylidene)-cyclohexanone) for the antioxidant properties in isoproteranol induced cardiac damage in mice. Also, in this study we have employed computational chemistry (semi-empirical PM3 method) on these symmetrical MACs with appropriate substituents with emphasis on electronic properties, atomic charges on the α,β-unsaturated system, torsional angle of the aryl group and especially the energy of the frontier molecular orbitals (HOMO and LUMO). This can be taken as a useful guide in the search for new compounds that may exhibit antioxidant and/or antinflammatory activity.

Keywords: synthesis, bioactivity, monocarbonyl analogs of curcumin, computational study.

OBPC P-39

SYNTHESIS AND STRUCTURAL STUDY OF (2*E*,6*E*)-4-*TERT*-BUTYL-2,6-BIS(2-BROMOBENZYLIDENE)CYCLOHEXANONE AND (2*E*,6*E*)-2,6-BIS(2-BROMOBENZYLIDENE)CYCLOHEXANONE

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(2*E*,6*E*)-2,6-bis(2-bromobenzylidene)cyclohexanone and (2*E*,6*E*)-4-*tert*-butyl-2,6-bis(2-bromobenzylidene)cyclohexanone belong to the group of conjugated compounds that contain electron withdrawing atoms, and might have potential use as NLO materials. These kind of compounds also have potential biological activities. To investigate their structural properties, synthesis was performed using crossed aldol condensation between 2-bromobenzaldehyde and cyclohexanone for the first compound, and 4-*tert*-butylcyclohexanone for the second one. The solid products were then further purified by recrystallization and powdered in order to perform further structural study. IR spectra were recorded using KBr pellets and ATR technique. It was established that the characteristic carbonyl (C=O) stretching frequency for (2*E*,6*E*)-2,6-bis(2-bromobenzylidene)cyclohexanone was at 1661 cm^{-1}, whereas for the (2*E*,6*E*)-4-*tert*-butyl-2,6-bis(2-bromobenzylidene)cyclohexanone it was at 1670 cm^{-1}. These two derivatives were also subjected to XRPD analysis and the data obtained was compared to other structuraly related derivatives. Computational methods were used to further investigate the structural features of these two derivatives with focus on the conformational effects versus solid state packing effects.

Analytical and Environmental Chemistry (AEC)

AEC O-1

CAPACITY OF CLADOSPORIUS CLADOSPORIOIDES FOR BIOREMEDIATION ENVIRONMENT CONTAMINATED WITH ETHOXYLATED OLEYL-CETYL ALCOHOL

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Not presented.

AEC O-2

LIGNOCELLULOSIC BIOMASS MAIN COMPONENTS STUDY THROUGH PYROLYSIS

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Biomass is a friendly alternative energy source widely spread in the nature, renewable and cheaper comparing to the fossil fuels. Pyrolysis can provide energy, fuel and chemical feedstock, i.e. gas, liquid/tar/oil, and char, making it a promising among the other biomass conversion processes. Lignocellulosic biomass is composed by three main organic components: lignin (10-25 wt. %), cellulose (40-60 wt. %) and hemicellulose (20-40 wt. %). Their ratio varies depending on the biomass type and part of the plant. In addition biomass contains inorganic compounds, low amounts of proteins, pectin and organic extracts. In the literature on this topic biomass components are studied in different aspects, but presently there is not a quantitatively systematic investigation on organic volatiles and products formed during pyrolysis of the lignocellulosic biomass. The role of these components in biomass pyrolysis process is not appreciated and their relative portion in products of pyrolysis is not estimated.

The aim of the present study was to receive quantitative information for the organic volatiles emitted during pyrolysis of the three main biomass components: cellulose, lignin and hemicellulose. Inasmuch as hemicellulose is hardly commercially delivered, it was replaced by xylan, often used in experimental as a representative substance of hemicellulose.

Atmosphere Pressure - Temperature Programed (AP-TP) technique coupled “off-line” with thermal desorption gas chromatography - mass spectrometry (TD-GC/MS) apparatus was successfully used to specify qualitatively and quantitatively organic functionalities in lignocellulosic biomass. Sample (*ca:* 25 mg) and 20 mg fumed silica are placed in the quartz reactor under a 100 ml/min flow of nitrogen. A linear temperature program of 10 °C min^{-1} from ambient temperature up to 900°C is applied. The outlet of the AP-TPR reactor is connected to a set of ice-cooled tubes containing Tenax (Sigma-Aldrich), a porous polymer of 2,6-diphenyl-*p*-phenylene oxide, as adsorbent. Volatiles were trapped in three temperature ranges in three different tubes: i) 250ºC÷600 ºC; ii) 600ºC - 800ºC and 800-900. Tenax tubes were separately desorbed and analyzed by TD-GC/MS instrument. Samples were spiked by d_4-thiophene, 3 μg, and d_{12}-chrysene, 0.5 μg, standards for data quantitative interpretation.

Pyrolysis has produced a complex mixture with a multitude of components, i.e. aromatics, furanes, lactones, phenols, acetic acid, etc. PAHs, i.e. naphthalenes, biphenyls, acenaphthilene, fluorene and their alkylated analogues were detected in the higher temperature region. Certain difficulties were depicted in the pyrograms: (i) cellulose volatiles were strongly dominated by 2-cyclopenten-1-ones, furanes and furaldehydes. A peculiar series of 5-Norbornene-2-carboxyaldehyde derivatives was depicted; (ii) in xylan volatiles were determined alkylbenzenes and phenols; (iii) lowest amounts and diversity was determined in lignin volatiles. Herein dominant were alkyl phenols, methoxy phenols, accompanied with some hydrocarbons pairs (nC_7-nC_{14}) and unexpected di- and trimethyl sulphides. The determined total amounts of volatiles for cellulose and xylan were comparable, 3060-3230 μg/g and considerably lower for lignin, 675 μg/g.

The study on the topic is in progress. It will continue with pyrolysis of cellulose, xylan and lignin mixtures at different proportions and comparison of the volatiles compositions.

Acknowledgements: The study is funded by NSF, Ministry of Education and Science under DN 04/5-2016 project and performed in the frame of BAS/FWO bilateral project.

Keywords: biomass, pyrolysis, volatiles, TD-GC/MS.

AEC O-3

ADVANCED SPATIAL MODELING FOR COPPER AND LEAD DISTRIBUTION DUE TO THE LONGTIME MINING ACTIVITIES

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The environmental concern in mining areas is primarily related to physical disturbanceof the surrounding landscape, mine tailings spill, emitted dust and acid mine drainage transported into rivers.The main purpose of this study was to develop a visualisation model of spatial distribution using linear and nonlinear mathematical methods that combine a sparsechemical analysis and various geospatial parameters in the Bregalnica River Basin, Kriva Reka River Basin, and the area of the field Ovče Pole, Republic of Macedonia.

Main problem of linear methods is that their concentrations depend only on distance. The most commonly used geostatistical prediction method is ordinary kriging that usea semivariance function.Various parameteres can influence the results what can lead to the wrong interpretation most common are Bull’s eye contours. In other side Artificial Neural Network – Multilayer Perceptron (ANN-MLP) improved much better results. ANN-MLP was used as nonlinear model for data processing and visualization of lead and copper in the investigated area. Model obtained by ANN was tested for the lithogenic (using top soil samples, 0-5 cm layer) distribution and atmospheric (moss samples) distribution. For the copper distribution enrichments were connected to the Cu open pit and some lithological units and along the rivers (alluvial planes) – what indicatative presence of river transport.Lead enrichment was connected only to Pb mining areas, some lithological units and along the rivers (alluvial planes). At the middle flow of the river Bregalnica the ANN didn’t isolated the high concentrations. This means that the sediments are trapped in the lake Kalimanci and polluted sediments accumulate in the lake. Atmospheric enrichment is also connected to the mining areas, while the high concentrations are not connected to the lithological units.

Keywords: Pb distribution, Cu distribution, ANN-MLP, mining, environmental distribution.

AEC O-4

REMOVAL OF TEXTILE DYE REACTIVE BLUE 19 FROM WATER BY NEW MESOPOROUS METAL SORBENT

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Environmental contamination by organic pollutants, as reactive textile dyes, has severe and chronic effects on living organisms [1]. Reactive Blue 19 (RB19) is one of the very stable and resistant anionic dye: it may be mutagenic and toxic because of the presence of electrophilic vinylsulfone groups [2]. The sorption has been frequently used for the removal of dyes from water because of its high efficiency, economic feasibility, and operational simplicity [3]. Layered double hydroxides as sorbents are characterized by high sorption capacity, low cost and non-toxicity.

In this study, co-precipitation synthesis of the mesoporous metal sorbent from Fe, Cu, Ni layered double hydroxide (FeCuNi-LDH), based on the data obtained from the thermogravimetric (TGA) analysis, was carried out for sorption of Reactive Blue 19 (RB19) [4]. The structure of the synthesized mesoporous metal sorbents (FeCuNi-280 and FeCuNi-550) and precursor (FeCuNi-LDH) were characterized by Brunauer-Emmett-Teller porosimetry method (BET). BET analysis shows that FeCuNi-280 (FeCuNi-LDH calcinated at 280°C) with mesoporous structure (166.84 m^2/g), has larger surface area compared to FeCuNi-LDH (93.85 m^2/g) and FeCuNi-550 (FeCuNi-LDH calcinated at 550°C) (25.10 m^2/g). The maximum sorption capacity of RB19 on FeCuNi-280 was 325.75 mg/g (the initial RB19 concentration of 200 mg/dm^3), while the maximum sorption capacity for FeCuNi-LDH and FeCuNi-550 was approximately 1.4 and 8.2 times smaller, respectively. Based on the determination coefficient and the relative deviation of calculated q_e and experimental q_e values, it has been deduced that the Sips model better fitted the experimental data and that the maximum sorption capacity amounted to 479.17 mg/g. The sorbent FeCuNi-280 showed better sorption capacity than all of the previously used sorbents for the removal of RB19 dye.

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Acknowledgments: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project TR34008).

Keywords: layered double hydroxide, triple-metal nanosorbent, reactive blue 19, isotherms.

AEC O-5

A REVIEW OF THE PRESENCE AND PROFILE OF PCB INDICATORS IN DIFFERENT ENVIRONMENTAL MATRICES IN ALBANIA

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Biomass is a friendly alternative energy source widely spread in the nature, renewable and cheaper comparing to the fossil fuels. Pyrolysis can provide energy, fuel and chemical feedstock, i.e. gas, liquid/tar/oil, and char, making it a promising among the other biomass conversion processes. Lignocellulosic biomass is composed by three main organic components: lignin (10-25 wt. %), cellulose (40-60 wt. %) and hemicellulose (20-40 wt. %). Their ratio varies depending on the biomass type and part of the plant. In addition biomass contains inorganic compounds, low amounts of proteins, pectin and organic extracts. In the literature on this topic biomass components are studied in different aspects, but presently there is not a quantitatively systematic investigation on organic volatiles and products formed during pyrolysis of the lignocellulosic biomass. The role of these components in biomass pyrolysis process is not appreciated and their relative portion in products of pyrolysis is not estimated.

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The study on the topic is in progress. It will continue with pyrolysis of cellulose, xylan and lignin mixtures at different proportions and comparison of the volatiles compositions.

Keywords: biomass, pyrolysis, volatiles, TD-GC/MS.

AEC O-6

DPP INVESTIGATION OF HEAVY METALS IN HONEY

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Differential Pulse Polarography was used to investigate heavy metals in environment through samples of honey. We collected samples in places, known to be industrial and samples of non industrial places, the last ones served us as a sample of comparison with the first ones. From the iterature data regarding the method, polarographic metal potentials showed us presence of heavy metals in honey where of : E_{cu}^{2+} = 86 mV, E_{Pb}^{2+}=-313 mV, E_{Cd}^{2+} = -503 mV. In our experimental conditions with these samples it was hard to detect the presence of Zn due to interference of hydrogen wave. From obtained polarograms for each metal calibration plots were constructed, where from we concluded the quantity of metals in analyzed samples, converted to mg/kg and afterwards shown in histograms.

Measurements were all conducted in a pure electrolyte HNO_3 at same conditions as in honey samples for metal concentration from $c_{(Me)} = 1 \cdot 10^{-7}$ mol/dm^3 – $1 \cdot 10^{-6}$ mol/dm^3 while the potential we followed was in the range from 0,25 – 0,8 V.

Keywords: Diferential Pulse Polarography, environmental pollution, heavy metals, honey.

AEC O-7

VOLTAMMETRIC DETERMINATION OF DOPAMINE AND URIC ACID IN SERUM USING ANIONIC SURFACTANTS AS A SURFACE MODIFIER OF CARBON PASTE ELECTRODES

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A selective and sensitive method was developed for the simultaneous electrochemical determination of dopamine and uric acid by using a sodium dodecylbenzenesulfonate (SDBS) and sodium dodecyl sulfate (SDS) as a surface modifier of carbon paste electrodes (CPE). At lower concentrations SDS and SDBS formed a negatively charged monolayer on CPE surface because of hydrophobic interaction of hydrophobic chain of surfactant and paraffin of CPE. Concentration of surfactants was 2 mM for SDS and 1 mM for SDBS on the phosphate buffer solution (0.1 M, pH = 7 and pH = 6, respectively). Compared with plain CPE, SDS-CPE and SDBS-CPE have shown improved electrochemical response of dopamine (DA) at 0.230 V and uric acid (UA) at 0.345 V due to electrostatic interactions between positively charged analytes and negatively charged SDBS and SDS. Under optimal experimental conditions, the designed electrodes exhibited wide linear responses to DA ranging from 0.53 μM to 105.0 μM and UA from 5.95 μM to 594.85 μM. The detection limits were found to be 0.26 μM and 1.25 μM for the determination of DA and UA (3s). The SDBS-CPE and SDS-CPE showed a good reproducibility, repeatability, stability and high selectivity for determination of DA and UA in blood serum.

Keywords: dopamine, uric acid, carbon paste electrode, SDS, SDBS, voltammetry.

AEC O-8

A NOVEL SPECTROPHOTOMETRIC METHOD FOR DETERMINATION OF FAMOTIDINE BY NITROSYL DERIVATE FORMATION

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A simple, rapid and sensitive spectrophotometric method has been proposed for determination of famotidine in pharmaceutical formulations. The new method is based on derivatization of famotidine to red color nitrosyl compound, which maximally absorbance appears at 490 nm. Different parameters were optimized based on intensity of produced color from derivatization conditions, such as reagent concentration, reaction time, sonification time, pH value, and temperature. Under optimized conditions Beer's law was obeyed in the concentration range up to 770 μg mL^{-1} with molar absorptivity 3.38 x 102 L mol^{-1} cm^{-1}. The limit of detection and limit of quantification were found to be 4.9 μg mL^{-1} and 16.4 μg mL^{-1}, respectively. The effect of studied interferents appeared to be negligible and this fact proved the good selectivity of the method. Method was successfully applied for determination of famotidine in tablets compared with HPLC method, thus demonstrating practical application of this method.

Keywords: famotidine, nitrosyl derivate, spectrophotometric, pharmaceutical analysis.

AEC O-9

TRICLOSAN IN WATER SAMPLES: ADJOINED EXPERIMENTAL AND THEORETICAL STUDY UNDER GC–MS CONDITIONS

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In the past years there has been growing concern of possible harmful consequences of exposure to xenobiotic compounds that are capable of modulating or disrupting the endocrine system of both wildlife and humans.

A water sample preparation method based on direct immersion single-drop microextraction (DI-SDME) followed by a conjoined gas chromatography – mass spectrometry (GC–MS) was used for the determination of a known endocrine disruptor, i.e. triclosan. 3 mL water samples spiked with appropriate amount of triclosan were extracted with a single (3 µL) drop of organic solvent. Extraction conditions, such as time and temperature were optimized. Derivatization, required for sensitive determination of this compound, on non-polar GC columns, was carried out using *N,O*-bis(trimethylsilyl)trifluoroacetamide inside the syringe barrel. Parameters affecting the derivatization reaction, such as temperature, time, solvent, and amount of reagent were studied. The established method was applied to water samples from Vardar River, tap water from different locations from Skopje as well as to samples from bottled water.

Chromatographic technique in this work includes the use of a mass spectrometer as a detector. Considering the possibility of simultaneous existence of a large number of conformational isomers and potentially different pathways of their breakdown under conditions of mass spectrometric experiments, we have performed a theoretical study of silylated derivatives of triclosan. In the present work the theoretical study was carried out by a conjoined static and dynamic approach, in which the density functional tight binding (DFTB) methodology is combined with molecular dynamics (MD) simulations.

Within the static approach, the corresponding potential energy surfaces (PESs) were explored in detail, and the located stationary points thereof were characterized by subsequent computations of the Hessian. Two real minima were located on the PESs of considered molecular system. To predict the finite-temperature behavior of the studied molecules, we performed MD simulations in the microcanonical (*NVE*) ensemble with the atom-centered density matrix propagation scheme (ADMP).

Keywords: triclosan, GC-MS, single-drop, DFTB, ADMP.

AEC O-10

METALLIC NANOPARTICLES FROM NATURAL MATERIALS: A RESEARCH OVERVIEW

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The present paper fully describes some of the most recent researches carried out by our team in the field of biosynthesized metallic nanoparticles from different plants and/or plant parts. Among the metallic nanoparticles, the focus is on silver (AgNPs) and gold (AuNPs) nanoparticles that are recognized for their antimicrobial, antifungal and antioxidant properties. Regarding the natural materials used as reducing agents, this research overview fully details the biosynthesis from Sea buckthorn (*Hippophae rhamnoides*), Gooseberry (*Ribes* grossularia), Ramson (*Allium ursinum*), Elderflower (*Sambucus nigra*) and Cornflowers (*Centaurea cyanus*), describing the two methods in our researches: (a) at room temperature, no stirring, overnight; (b) at 50^0 C, 450 rpm, 30 minutes. The formation of both AgNPs and AuNPs was studied by different physical-chemical techniques: UV-Vis, FTIR, microscopy, DLS, TEM, etc.

Keywords: metallic nanoparticles, biosynthesis, natural materials.

AEC P-1

AN EXPERIMENTAL DESIGN APPROACH IN OPTIMIZATION OF AN EXTRACTION PROCEDURE FOR AAS DETERMINATION OF Ca, Mg, Zn, Cu AND Fe IN MULTIMINERAL DIETARY SUPPLEMENTS

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Jelena Acevska[1], Natalija Nakov[1], Zoran Kavrakovski[1], Aneta Dimitrovska[1],
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Sample preparation, as the most sensitive and time-consuming step in AAS, can be usually performed by digestion or extraction methods. Compared to digestion methods, extraction is simpler, safer, cheaper and represents a valuable alternative to laboratories that lack the possibility of having expensive equipment and instrumentation (Longas et al., 2009; Paula et al., 2013). The application of experimental design approach for optimization of the extraction procedure, compared to univariate approach, offers the advantages of simultaneous evaluation of several experimental conditions, performing smaller number of experiments (Soriano et al., 2007a; Kenduzler et al., 2008).

The aim of our study was application of experimental design approach in optimization of ultrasonic stirring acid extraction of Ca, Mg, Zn, Cu and Fe in multimineral dietary supplements followed by determination using FAAS.

The influence of ultrasonic extraction time (10 - 30 min), temperature (20 – 60 ˚C) and HCl concentration (1.0 -5.0 mol L^{-1}, extraction solution) was investigated using full factorial 2^3 design (MODDE 10.0). The selection of experimental variables was performed considering the study of Soriano et al., (Sorriano et al., 2007b). Experimental response (extraction efficiency) was evaluated by calculation of element's recovery after extraction. Ultrasonic stirring extraction was performed using 150 mg sample and 10 ml of extraction solution. The determination of the mineral content was performed on Shimadzu AA-7000 atomic absorption spectrometer.

The analysis of Contour plots of experimental responses using Response Surface Methodology (RSM) has shown that optimal recovery for the studied elements is obtained when HCl concentration is 3.0 mol L^{-1}, the extraction temperature is 25 ˚C and the ultrasonic extraction time is 30 min. Also, this investigation showed that the ultrasonic extraction time and the temperature had higher influence on the extraction process, compared to the influence of acid concentration. The optimized method was validated in terms of linearity, accuracy and precision, limit of detection and limit of quantification. The application of experimental design approach enabled a simple and a reliable method for determination of Ca, Mg, Zn, Cu and Fe in multimineral dietary supplements.

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Keywords: experimental design; ultrasonic extraction; AAS; multimineral supplements.

AEC P-2

INFLUENCE OF FLUOROQUINOLONE ANTIBIOTICS ON BIOSPECIATION OF IRON (III) ION IN HUMAN BLOOD PLASMA

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Fluoroquinolone (FQ) family drugs are frequently used to treat various bacterial infections due to their antibacterial activity against Gram-positive and Gram-negative bacteria pathogens [1]. The ability of FQs to compete with plasma metal ions and with other low molecular weight (LMW) ligands can be assessed in term of the plasma mobilizing index (PMI) proposed by May and Williams [2]. This index can be used to define mobilization power of FQs to the metal ions in blood plasma. The PMI of particular metal ion is defined as the ratio of the total concentration of LMW-metal species in the presence and absence of the exogenous ligand in blood plasma. This is a useful tool to carry out preliminary in vitro assessment of mobilizing influence of chelating agent using computer modeling based on the thermodynamic data for the equilibria occurring in blood plasma.

In this work influence of some fluoroquinolones (levofloxacin, ofloxacin, ciprofloxacin and moxifloxacin) on biospeciation of main Fe (III)- LMW complexes in blood plasma studied using program HySS^{2009}. For simulation purpose the complex formation between iron (III) ion and FQ was studied by potentiometric titration at physiological condition and stability constants were calculated with Hyperquad^{2006} program suite. In our previous work we improved a literature blood plasma model using HySS2009 software, taking into account 9 metal ions, 45 ligands, generating more than 6100 complexes [3]. To this model, the complexes with FQ were added. To estimate the complexation ability of these antibiotic agents *in vivo* with iron(III) ion, their plasma mobilizing indexes (PMI) were calculated.

The PMI curves of iron(III) ion with studied FQs are shown in Figure 1. Mobilization of iron(III) ion by FQs does not occur at ligand concentration less than 1×10^{-5} molL^{-1} (which is a therapeutic concentration). Results obtained from HySS2009 calculation indicate that FQs below the concentration of 10^{-5} molL^{-1} are dominantly bound into the calcium and magnesium complexes while iron(III) ion is mainly bound to the citrate complex (~ 99%) . From Figure 1 it can be seen that mobilization of iron ions is the most significant with moxifloxacin while other FQs show the order moxifloxacin > levofloxacin > ofloxacin > ciprofloxacin. This results indicate that fluoroquinolones at therapeutic concentration does not affect the biospeciation of iron(III) ion in blood plasma.

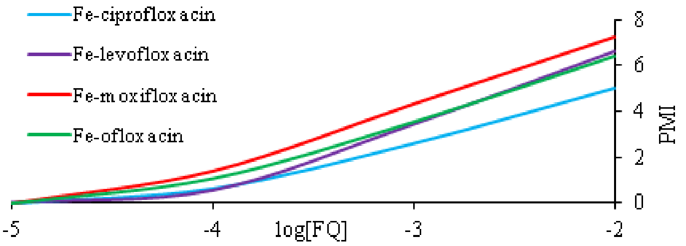

Figure 1. PMI curves of Fe(III) ion - Fluoroqiunolone systems

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Keywords: fluoroquinolone, antibiotics, biospeciation, Fe(III) ion.

AEC P-3

IMPACT OF OIL EXTRACTION AND PROCESSING INDUSTRY IN SURFACE WATERS. CASE STUDY: PATOS-MARINZA AREA, ALBANIA

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This study presented data about concentrations of n-Alkanes (C10-C26), PAH (Polycyclic Aromatic Hydrocarbons) and BTEX (Benzene, Toluene, Ethylbenzene and o-, m-, p-Xylenes) in surface water ecosystems of Patos-Marinza area, Albania. This area is located in central Albania. It is known for oil extraction and processing industry for more than 80 years. Water samples were collected in sixteen stations in December 2017. The stations were selected in Patos-Marinza area for some streams and two rivers (Semani and Gjanica rivers) that could be affected from oil industry.

For isolation of PAH liquid-liquid extraction assisted with n-Hexane as extraction solvent were used. 1 L water samples were taken for each stations of Patoku Lagoon for n-Alkanes and PAH analyze. Headspace solid phase micro extraction (HS-SPME) technique was used to trace BTEX in water samples. The analysis of n-Alkanes, PAH and BTEX in water samples was performed by gas chromatography technique using flame ionization detector (GC/FID). Injections of BTEX were done in injector PTV directly by using Head-Space mode of Polydimethyl Siloxane fiber. 1 ul extract in n-Hexane (extracting solvent) were injected for n-Alkanas and PAH analyses. VF-1ms capillary column (30 m x 0.33 mm x 0.25 um) was used for separation of n-Alkanes, PAH and BTEX compounds.

Relatively high concentrations of BTEX and more volatile PAH compounds were detected in water samples of Patos-Marinza area. The presence of hydrocarbons shows impact of oil extraction and processing industry in surface waters of this area. Note that these levels could be momentum values connected mainly with solubility of each individual hydrocarbon. Analyze of hydrocarbons must be monitored for a longer time because of oil industry impact must be higher in this area. The dilution factor could be higher in December because of great amount of rainfall in this period.

Keywords: n-alkanes, PAH, BTEX, LLE, HS-SPME, GC/FID, water analyze, Patos-Marinza.

AEC P-4

QUALITY CONTROL AND QUALITY ASSURANCE IN ANALYTICAL LABORATORY

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Department of Testing analytical laboratories provides quantitative analysis of forest ecosystem components, the main nutriens such as S, C, N, P, K, Ca, Mg and also metalic elements like Al, Fe, Mn, Zn, Cd, Cu are determined in all parts of forest ecosystem by modern instrumental techniques. Most of the results is used by experts from Department of Forest ecology for long- time monitoring of health state of forests in Czech Republic under the International Cooperative Programme on Assesment and Monitoring of Air Pollution Effects on Forests – ICP Forests. Therefore, the analytical proces producing output data has to be kept stable in time (quality assurance) to make results comparability possible. Data quality assurance (QA) and quality control (QC) procedures are applied in laboratory measurements to check and confirm quality of laboratory work, the different ways (in-house or outside such as control charts for blanks, control sample, duplicate samples, traceability by using certified reference material, interlaboratory comparison) of quality control are used. Quality of laboratory measurement is influenced by many random and systematic effects which can be uncovered during validation procedure and its knowledge is very important for the evaluation of uncertainty and finaly expanded uncertainty, important specification of every result of measurement.

Keywords: forest ecosystem, chemical analysis, quality control.

AEC P-5

THE ADSORPTION OF PESTICIDES THROUGH TITANIUM DIOXIDE PARTICLES GRAFTED BY SUBSTITUTED PHENYL LAYERS

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The present research focused on the feasibility of using non-toxic materials such as titanium dioxide microparticles (TiO_2) for the absorption of chlorinated pesticides. Batch experiments were conducted to evaluate the effects of the adsorbent dose, contact time, mass and stirring speed on the adsorptive behaviour of this adsorbent toward the Aldrin pesticide. The sorption process is accomplished using as sorbent: bare and covalently grafted titanium dioxide microparticles with different organic layers such as carboxyphenyl and phenyl layers. The adsorption process is assessed using cyclohexane as a solvent.

The adsorption study included different adsorbent quantities (10, 30, 70 and 100 mg) using the same contact time of the adsorbent and the pesticide solution. The synthesized diazonium salts and modified Titanium dioxide were analyzed by ATR spectroscopy (on diamond crystal). GC-ECD is used to assess and compare the adsorptive properties of the used materials (bare or modified TiO_2).

Monte Carlo calculations were used in order to gain profound insights vis-à-vis the surface interaction between the Aldrin molecule and the adsorbent.

Keywords: Titanium dioxide, Aldrine, diazonium salts, adsorption, GC-ECD.

AEC P-6

SURFACE MODIFICATION IMPACT ON THE GRAPHENE OXIDE ADSORPTION PERFORMANCE TOWARD THE ALDRIN® MOLECULE

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Graphene oxide (GO) has recently attracted immense interest in material science because of its unique properties such as large surface area, mechanical stability, tunable electrical and optical properties. The surface functional groups such as hydroxyl, epoxy, and carboxyl have increased the use of graphene oxide in different fields and the opportunities for GO modification.

The synthesis of graphene oxide was completed by using Hummers through the addition of $KMnO_4$. Substituted aryl amines were used for the synthesis of the aryldiazonium by using a sodium nitrite a diazotizing reagent. The surface modification of Graphene oxide was performed by using the radicals derived from aryldiazonium salts (by ultrasonication).

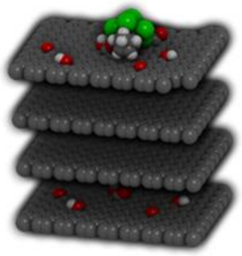

Figure 1. The 3D model of the Graphite Oxide with the adsorbed Aldrin molecule.

The synthesized diazonium salts, graphene oxide and modified graphene oxide (with phenyl, iodo-phenyl and nitro-phenyl groups) were analyzed by ATR spectroscopy (using diamond crystal).

GC-ECD is used to assess and compare the adsorptive properties of the used materials (bare or modified Graphene oxide). The surface modification of the GOx has a strong impact on the adsorption behavior of GOx toward Aldrin pesticide.

Keywords: Graphene oxide, Aldrine, diazonium salts, adsorption, GC-ECD, molecular mechanics.

AEC P-7

TAILORING THE GRAPHENE SURFACE THROUGH THE COVALENT GRAFTING OF SUBSTITUTED ARYL GROUPS. A PESTICIDE ADSORPTION STUDY

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Graphene has attracted the interest of chemists, physicists, and materials scientists due to its extraordinary structural, mechanical, and electronic properties. It has been evidenced that the potential applications of graphene can be extensively expanded by various modes of functionalization, including non-covalent binding (adsorption) of molecules and nanoparticles. Many applications require modified or functionalized forms of graphene, such as graphene oxide, reduced graphene, or other functionalized forms. Structurally modifying graphene through chemical functionalization reveals the numerous possibilities for tuning its structure.

This study involved the synthesis of graphene, aryldiazonium salts and modification of graphene by using diazonium salts. Exfoliation of graphite is a promising approach for large-scale production of graphene. The synthesis of RGO was done by sonication-assisted oxidation of graphite in a solution of potassium permanganate and concentrated sulfuric acid followed by reduction with ascorbic acid prior to any washing processes. GO loses its hydrophilicity during the reduction stage which facilitates the washing step and reduces the time required for the production of RGO.

Surface modification of materials through the grafting of the aryl diazonium salts represents an easy and flexible strategy that enables covalent modification of a wide range of materials such as metals, semi-conductors, polymers, semi-conductors, metals, etc. This strategy permits to tailor the interface of the materials by a widespread number of the functional groups that reflect different physicochemical properties to the surface of the material.

The surface modification of graphene was performed by using three different synthesized aryldiazonium salts (p–iodo, –nitro and benzenediazonium tetrafluoroborate). The modified surface was successfully applied for the adsorption of Aldrin from cyclohexane solution. For the assessment of adsorptive properties of the analyzed materials, GC-ECD chromatography technique was used. Prior to the adsorption studies, the synthesized diazonium salts, graphene and modified graphene (by phenyl, iodophenyl and nitro-phenyl groups) were analyzed by FT-IR or ATR spectroscopy (Attenuated Total Reflectance) technique using diamond crystal. Furthermore, we used molecular mechanics to calculate the total energy of the systems by running optimization algorithms through the use of force-fields.

The purpose of this research is the investigation of the ability of graphene and modified graphene on the absorption of chlorinated pesticides, respectively Aldrin, from the organic solution (in cyclohexane).

Keywords: Graphene, Aldrin, adsorption, diazonium salts, GC-ECD, FT-IR, ATR, molecular mechanics.

AEC P-8

TUNING THE ADSORPTION PERFORMANCE OF GRAPHITE FLAKES THROUGH COVALENT SURFACE MODIFICATION WITH SUBSTITUTED PHENYL LAYERS DERIVED FROM DIAZONIUM SALTS

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Despite their global ban, organochlorine pesticides have been a persistent and significant environmental health issue worldwide. The presence of pesticides in the environment is a concern that needs to be addressed and solved because these molecules possess a high degree of toxicity.The objective of this research was the investigation of the ability of graphite flakes and modified graphite on the absorption of Aldrin (an organochlorine pesticide). In order to tailor the properties of these particles prior to use for the surface modification, the synthesis of the diazonium salts was performed. The study involved the synthesis of two aryl diazonium salts bearing nitrophenyl and carboxyphenyl moieties. This surface modification strategy involves the generation of very reactive radicals by dediazoniation of the aryldiazonium [1]. The formed radicals are prone to form covalent bonds to the surface, enabling a simple way for surface tailoring. In the synthetic step, the corresponding substituted anilines (4-aminobenzoic acid or 4-nitroaniline) were dissolved in aqueous HBF_4 and then diazotized by addition of sodium nitrite. Materials which were used as adsorbent were: Graphite flakes and graphite flakes modified by either p-nitrophenyl or p-carboxyphenyl layers.

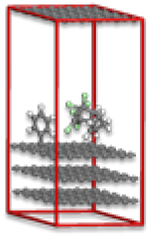

Figure 1. Slab model of modified graphite surface (with phenyl layers) used in the Monte Carlo simulations.

GC/ECD was used to confirm the ability of the bare and modified graphite flakes toward the adsorption of the Aldrin molecule. This is important and could be used to develop a new eco-friendly strategy for pre-concentration (for the analytical purpose) or removal of pesticide. Monte Carlo simulations (Figure 1) were applied in order to gain insights at molecular level regarding the adsorption of this molecule.

Keywords: Graphite, Aldrin, diazonium salts, adsorption, GC-ECD.

AEC P-9

NEUTRON ACTIVATION ANALYSIS, k_0-STANDARDIZATION METHOD, AT SERVICE OF HEALTH DETERMINING IMPURITIES IN FOOD

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Neutron Activation Analysis (NAA) is a multielemental analytical technique to assay the elemental chemical composition in samples of several matrices. This technique was established at the Nuclear Technology Development Centre (Centro de Desenvolvimento da Tecnologia Nuclear) sponsored by Brazilian Commission for Nuclear Energy, CDTN/CNEN, located in Belo Horizonte, Minas Gerais, in 1960, just after the start-up of the TRIGA MARK I IPR-R1 research nuclear reactor. The first application of the technique was the Delayed Fission Neutrons Analysis to determine uranium in ore in pyrochlore, a niobium ore that would be exported, during the mineral prospecting of uranium ore in Brazil. Until 1994, only Delayed Fission Neutrons and Relative Neutron Activation Analysis, including Instrumental and Radiochemical methods, were applied. In 1995, the k_0Instrumental Neutron Activation Analysis was established at CDTN, due to the growing need to determine several elements in a unique sample meeting the clients' analytical needs and researches [1].

In 2003 the k_0-standardization method was introduced successfully [2]. Since then, the method has been applied in diversified matrices as soil, sediment, ore, biomaterial – human tissues (hair, nails) and fluids, animal tissues (muscle, liver), plant (vegetable, pasture, fruit, etc.) - air filters, solid waste, industrial residue, petroleum, stainless steel, several precipitates, archaeological ceramic, and others. This method is a non-destructive analysis – it is not needed to solubilize the sample – and uses neutron flux monitors instead of standards and the nuclear data which are unknown are replaced by compound nuclear constants characterising the nuclides, k_0 factors. It is required good knowledge of spectral parameters of the neutron flux in irradiation channels of the nuclear reactor.

One very important and well succeeded application is determining several chemical elements in food [3,4,5]. The objective is not only to determine essential elements but also impurities or contaminants. This contamination is a matter of serious consideration because it poses health risks. The impurities could be due to naturally occurring in the environment or from anthropogenic sources. The steps of food processing, packaging, transportation, and storage are also significant contributors to impurities or contamination and these impurities are not taken into consideration by food composition databases. These databases are very useful in assessing the quality of nutritional intake of individuals and populations, but they are usually quite deficient in relation to components such as bioactive compounds, contaminants and trace elements [6,7]. Examples of some food - sugar, dietary supplements and whole food - analysed by k_0-standardization method at CDTN is showed and the results are discussed in this paper. Reference materials were also analysed and the performance of the method was evaluated by the statistical test E_n-score, ISO 13528:2015(E), Statistical Methods for use in Proficiency Testing by Interlaboratory Comparison, pointing out the reliability and versatility of the method.

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Keywords: neutron activation analysis, k_0-standardization method, food.

AEC P-10

POTENTIAL ORGANIC POLLUTANTS FROM CORE SEDIMENT SAMPLES, TROYANOVO-1 MINE, MARITSA IZTOK LIGNITE BASIN, BULGARIA

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The environmental problems posed by inorganic constituents of coals, sediments, dump materials, etc. are well documented based on sensitive and highly productive techniques' application. On the contrary, the low content and comparatively expensive, continuous and complicated process of isolation, fractionation and identification leaded to a systematic ignoring of the organic constituents. Nowadays with the increase in precision of instrumental techniques the handling and control of harmful organic compounds, i.e. in wastes of energy production, became important of ecological concern.

Mini Maritsa Iztok EAD is the main coal mining company in the Republic of Bulgaria. Lignite reserves in the basin, used as a source of electric power generation, are projected to last for at least the next 50-60 years. Mining works in the basin have produced a huge volume of dump waste materials that could provoke a potential threat to cause environmental problems during weathering and subsequent leaching of organic pollutants.

In the present study our attention is stressed on log core sediment samples, integral constituents of dump materials. Sediments concern materials excavated and removed by continuous operation of bucket wheel excavators, transported by rubber-belt conveyors and free-heaped by belt spreaders *(www.marica-iztok.com)* in a dump area, i.e. artificially reworked and redeposited sediments.

Seven core samples of carbonaceous mudstones from Troyanovo-1 Mine, Maritsa Iztok Basin, Bulgaria occupying depth interval 54.00 - 91.00 m were analyzed by geochemical proxies. Briefly, samples (*ca.* 40 g) were extracted by chloroform (~300 ml), under reflux for 30 h. Chloroform-soluble portion (SOM) was concentrated and asphaltenes were precipitated. The soluble components (maltenes) were subsequently separated *via* column chromatography. Mini-glass column (10×1 cm) with Kieselgel (35–70 mesh ASTM) was used. The following fractions were prepared: neutrals, aromatic/slightly polars, and heteroatom containing NOS. Subsequently the first two fractions were studied by gas-chromatography-mass spectrometry (GC-MS). Organic pollutants were tracked in aromatic/slightly polars.

The identified organic compounds with a potential environmental impact were quantified and normalized per g TOC of sediment and recalculated for kg of sample. Some differences in total pollutant contents with depth were depicted. Main components registered and quantified were: phthalates (dominant), *i*-propyl palmitate, *i*-propyl myristate, benzoates, etc. The ranges for the tracked organic pollutants, in mg/kg core sediment, were determined: phthalates – 1-17; tetrachloroethane - < 1; *i-Pr* esters of fatty acids - < 1; benzoates - ~ 2; benzones – 1-2; phenol - < 1;/. All listed organic contaminants are interpreted as anthropogenic (originating from plasticizers, industrial pollutants, solvents, etc.) excepting phenol with natural origin. At the moment there is not any reliable explanation for their presence inasmuch all acquired precautions for samples contamination have been applied. However, even in very low amounts these organic pollutants should be under controls as the problem for human health is not in their absolute concentrations but in the long exposure to their harmful impact.

Acknowledgements: The study was funded by NSF, Ministry of Education and Science under DN 04/5-2016 project.

Keywords: Maritsa Iztok Basin, core sediments, organic pollutants.

AEC P-11

NUCLEAR TECHNOLOGY DEVELOPMENT CENTRE, BELO HORIZONTE, BRAZIL: ENVIRONMENTAL MONITORING PROGRAM

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Several activities are carried out by CDTN' departments - Nuclear Technology Development Centre, an institution located at Belo Horizonte city, the capital of Minas Gerais, a Brazilian State. Diversified liquid effluents, radioactive and non-radioactive waste can be generated by the activities carried out. Due to this, there are several potential sources of environmental contamination. These sources should be monitored and controlled otherwise they may cause direct and indirect risks to man and the environment. Due to these risks, the Environmental Monitoring Program (EMP) has been operating since 1985, aiming at evaluating and controlling the installations' operating conditions. The impact caused by release of stable and radioactive elements on the surrounding environment is, then, continuously evaluated. The EMP for radioactive and nuclear installations is based on Regulatory Position 3.01/008 "Environmental Radiological Monitoring Program" [1] from the Brazilian Nuclear Energy Commission that establishes the main requirements for development of an operational EMP.

CDTN's EMP includes sampling of liquid effluent, particulate airborne matter, soil, vegetation, surface water, sediment, and groundwater and radionuclides are determined in these samples. Besides data collecting, a continuous and systematic follow up process of environmental variables should be done as well as to qualitatively and quantitatively identify and evaluate the conditions of natural resources at a specified moment and the tendency over time. In 2002, the institute received IBAMA (Brazilian Environmental and Water Resource Institute) [2] Environmental Operation License. From this time on, other parameters started to be monitored by law.

According to legislation, chemical analyses include determination of gross alpha and gross beta activities, concentration of activities of the natural radioactive elements ^{40}K, ^{210}Pb, ^{226}Ra, ^{228}Ra, ^{238}U, and ^{232}Th, concentration of oil and grease, ammonia, barium, cadmium, copper, total chromium, hexavalent chromium, mercury, silver, and nickel, as well as physical-chemical parameters, pH, temperature, and conductivity. Analytical methods applied depend on the analyte and matrix and techniques as AAA, ICPMS, HPLC. Radioactive elements are measured by neutron activation analysis, gamma spectrometry and liquid scintillation.

This work shows that the results are in good agreement with Brazilian legislation pointing out that the EMP is an efficient tool to prove that the CDTN's activities are not contaminating the environment.

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Keywords: environment monitoring, radionuclides, analytical techniques.

AEC P-12

THE EFFECT OF THE SURFACTANTS ON THE ELECTROCHEMICAL DETECTION PERFORMANCE OF THE VITAMIN C

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Vitamin C, also known as L-ascorbic acid, is a water-soluble vitamin present naturally in some foods, added to others, and available as a dietary supplement. Humans, in contrast to most of the animals, are incapable to synthesize vitamin C endogenously, so this molecule it is an essential dietary component. The determination of Vitamin C in different samples has enormous importance and is frequently accomplished through the HPLC, UV-VIS, electrochemical methods, etc. The electrochemical determination of vitamin C was done using cyclic voltammetry on a Palm Sens (potentiostat/galvanostat) instrument. The experiments were performed in a conventional single-compartment three-electrode cell. A Platinum electrode was employed as a working, Platinum foil as an auxiliary electrode and Ag/AgCl served as a reference electrode. The calibration curves were constructed in the vitamin C solution: a. in absence, b. in presence of 5% Triton X-100 or c. 10% Methanol at the concentration range from 1mM up to 600 mM. The addition of surfactants increases the sensitivity for the determination of this molecules. The electrochemical determination was successfully applied for the determination of the content of this molecule in different samples.

Keywords: cyclic voltammetry, vitamin C, surfactants, limit of detection.

AEC P-13

AUTHENTICITY ASSESMENT AND QUALITY CONTROL OF CROATIAN HONEYDEW HONEYS ON THE BASIS OF MULTI-ELEMENT ANALYSIS WITH CHEMOMETRIC APPROACH

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Regarding the importance of consumption of honey with proven health-beneficial properties, high sensory values and rich composition in bioactive substances, the aim of this study was to estimate authenticity and quality of honeydew honeys according to their mineral and heavy metal composition. Twenty one elements were determined in 64 honeydew honey samples of five different botanical origins (silver fir (*Abies alba* Mill.), evergreen oak (*Quercus ilex* L.), Hungarian oak (*Quercus frainetto* Ten.), Montpellier maple (*Acer monspessulanum* L.), conifers), from several part of coastal, mountain and continental area of Croatia. Inductively coupled atomic plasma emission spectrometry was used for the determination of Al, Ca, Fe, K, Mg, Na, P and S, while inductively coupled plasma mass spectrometry was used for the determination of As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, Sr and Zn. Data of elemental analysis allowed the discrimination and classification of honeydew honeys in accordance to their botanical origin using pattern recognition techniques. The analytical data also indicated a good level of quality of honeydew honeys, especially with regard to the concentration of toxic elements.

Keywords: Honeydew honey, elements, botanical origin, multivariate techniques, consumer protection.

AEC P-14

WATER AS A MILD EXTRACTANT OF METALS AND METALLOIDS FROM SOIL SAMPLES

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Soil is a very complex component of an ecosystem and is highly exposed to potential input of the toxic substances. Soil is a very powerful reservoir of such substances due to its ability to bind various chemicals onto the surface of the soil particles [1]. Trace metals and metalloids are amongst such substances. Potential hazard of an elevated presence of toxic elements in soil lies in the fact that chemical elements, in their various chemical forms, can enter food chain. The main input of the toxic elements into food chain is through their uptake by plants [2].

An assessment of mobility and bioavailability of trace elements that are present in soil requires determination of those elements in soil samples by an appropriate methodology. The most of the methods for trace metals and metalloids analysis in the soils samples, that are described in the scientific literature and present in wide professional practice, consist of a transfer of the analytes into solution with subsequent quantification of the elements in the prepared solutions (extracts or digestates) by mean of some of the atomic spectrometric techniques. Furthermore, the most applied method of transferring of the metals and metalloids into solution includes digestion of the tested soil samples by *aqua regia* [3]. Such an aggressive digestion medium do not simulate natural conditions in soil and, yielding too high concentrations of the elements in the digestates, does not allow to draw reliable conclusions about mobility of the analyzed elements in soil. Therefore, many researchers are occupied with developing and characterization of the methodologies that would be better in terms of making assessments of bioavailability of the elements of ecological interest. Namely, the use of mild extraction reagents is much more appropriate [4].

This work describes the analysis of 27 selected chemical elements (Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Sr, Ti, Tl, V, and Zn) in three selected certified reference materials (CRM) for soil. The extraction of the elements from CRM samples was made by deionized water at room temperature. The reaction mixtures (~1 g soil sample / 10 mL H_2O) were shaken on the orbital shaker for 24 h. The samples were filtered (0.45 μm), acidified (HNO_3, *supra pur*, $\psi = 1$ %), and the concentrations of the selected elements in the prepared extracts were measured by inductively coupled plasma – atomic emission spectrometry (ICP-AES).

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Keywords: soil, mild extraction, trace elements, major elements, ICP-AES.

AEC P-15

MULTI-ELEMENTAL CHARACTERIZATION OF CROATIAN BOTTLED WATERS BY ICP-AES

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Water is an essential substance for all living organism and it is a source of various nutritive substances. Natural water, *i.e.* water that is free of the products of human activities, generally reflects the geochemistry of the environment through which it flows [1]. At the same time, water is at risk of pollution due to various human activities, such as industry or traffic. Awareness of the endangering of natural water resources as well as knowledge about leaching of some heavy metals from plumbing system (e.g. Cu, Ni, Pb) [2], resulted, among others, in the interest of people all around the world in everyday use of bottled, commercially distributed, water. Along with the production and consumption of bottled water, that are permanently increasing, an interest of the researchers in testing of the commercially distributed bottled waters has been occurring worldwide during the past several years and a survey of scientific database *Web of Science* reveals that scientific papers dealing with the results of various testings of bottled waters are regularly published.

Bottled water can be of natural origin, or its qualitative and quantitative composition can be regulated by processing in a production plant. Therefore, metals and metalloids content of a bottled drinking water can reflect geochemistry of its origin, but can also, intentionally or unintentionally, introduced during the production process, filling of bottles, *etc.* Also, some elements can be leached from the material of a bottle. Thus it is well known that aluminium (Al) or lead (Pb) can be leached from glass bottle into water [3], while from PET bottles the leaching of antimony (Sb) occurs [4].

In this work, determination of ca. 20 selected chemical elements (Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Sr, Ti, Tl, V, Zn) in the bottled waters of different brands was performed. For this communication, only those bottled waters which are labeled as "product of Croatia" were analyzed: 19 brands of still and sparkling water were included in the study. The samples were randomly taken from various supermarkets in the town of Zagreb, with the intention to find as much as possible various Croatian brands of bottled drinking water. Determination of almost all elements was done by direct measurement of the previously acidified (HNO_3, *supra pur*, $\psi = 1$ %) samples of the waters by mean of atomic emission spectrometry with inductively coupled plasma (ICP-AES), while calcium was measured in 100-fold diluted sample solutions.

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Acknowledgements: Development Fund of the University of Zagreb.

Keywords: bottled waters, ICP-OES, heavy metals, trace elements, major elements.

AEC P-16

THE PRESENCE OF SOME HEAVY METALS (Cu, Pb, Cd AND Zn) IN HONEY SAMPLES COLLECTED IN INDUSTRIALIZED REGION OF MITROVICA (KOSOVO)

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Honey has a higher nutritional value and it is a composition of carbohydrates, acids, minerals, flavonoids, vitamins, waxes, aroma compounds, etc. This composition depends on the nectar and honeydews which is strongly influenced by the pollution of the ecosystem. Thus, the analysis of honey for heavy metals (a frequently encountered environmental pollutants in industrialized area) is of outmost importance due to a strong consumption of honey. The heavy metals in honey are of interest for quality control to ensure that the contamination are below the concentration that is harmful. In this work we analyzed the concentration of several heavy metals (copper, lead, zinc and cadmium) in honey samples used as a bioindicator for the environmental pollution of the studied area. The collection of honey samples was performed in different locations at the Industrial region of Mitrovica. The Differential Pulse Anodic Stripping Voltammetry (DPASV) is used as analytical technique for the heavy metal determination. The measurements were performed in Briton-Robinson buffer solution at pH~2.1 using different deposition times (ranging from 0 s to 120 s) for metal ions at the mercury electrode. The used potential range for stripping the accumulated metal was +200 mV to -1500 mV. The result shows that the concentration of heavy metals in honey samples were in the range: 0.15-0.49 mg/kg for Cu; 0.27-1.7 mg/kg for Pb and for Cd from 0.06-0.34 mg/kg. From the data analysis, the presence of lead and cadmium in some of the honey samples exceeded the allowed values for these metals.

Keywords: heavy metals, honey, differential pulse anodic stripping voltammetry, environmental pollution.

AEC P-17

THE USE OF LEMON PEELS AS AN ADSORBENTS FOR HEAVY METALS

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Environmental pollution represents a problematic and a vast challenge for the society in the 21st century. A particular type of pollutants that are found widespread in many areas as a result of increased industrial activity are toxic metals. In our work we evaluated the adsorption properties of lemon peel as biosorbent material for the removal of several heavy metals ions, including: Cu(II), Pb(II), Cd(II) and Zn(II) from the aqueous media at different concentrations. The amount of adsorbent is changed from 10 to 100 mg. The lemon peels were also activated using nitric acid or sodium hydroxide ($C = 0.4$ M). The evaluation of the sorption properties of the used bio sorbent is done by using Differential Pulse Voltammetry (DPV) – at the mercury electrode. The pH value has strong influence on the sorption ability of the material, the increase of the pH value from 1.5 to 5.5 leads to higher sorption amounts for the heavy metal ions. The results show that the use of this material as bio sorbent is very promising as it is cheap, eco-friendly and nontoxic waste material.

Keywords: adsorption; heavy metals; environmental pollution; Differential Pulse Voltammetry (DPV).

AEC P-18

THE INFLUENCE OF SOME PYRAZOLE DERIVATIVES AND NEWLY SYNTHETISED Cu(II), Ni(II) AND Zn(II) COMPLEXES TO THE INHIBITION OF *Phomopsis viticolamycelium in vitro*

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Pyrazole-based compounds and their transition metal complexes have attracted considerable research interest because of their potentially beneficial biological properties. The wide biological activity of this class of compounds (anticancer, antimicrobial, antiviral, anti-inflammatory, antifungal and others) is described in several reviews [1-4]. These results represent a part of our continued work with pyrazole based complex [5-6].

In the study, inhibitory effects of newly synthesizedCu(II), Ni(II) and Zn(II) complexes obtained in reaction $Cu(OAc)_2$, $Ni(OAc)_2$and $Zn(OAc)_2$, with 4-Bromo-2-(1H-pyrazol-3-yl)phenol (HL) were examined to the mycelial growth of *Phomopsis viticola*(pathogenic fungus that causes Phomopsis cane and leaf spot disease of grapevine) *in vitro*. The compounds were applied in five 5 different concentrations, ranged from 0.12 to 0.0075%. Obtained results were compared with the commercial fungicide which one active substance is pyraclostobin that belongs to pyrazole derivates. All examined compounds expressed significant effect on mycelial growth.

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Acknowledgements: This research was conducted within the innovation project: „Study on biological efficacy of newly synthesized compounds and plant extract to the most important diseases of grapevine in Montenegro"supported by Ministry of Science of Montenegro.

Keywords: 4-Bromo-2-(1H-pyrazol-3-yl)phenol; complexes of Zn, Ni and Cu; Phomopsis viticola; active fungicidal substances, Phomopsis cane and leaf spot disease of grapevine.

AEC P-19

SPECTROPHOTOMETRIC ZINC(II) BASED DETERMINATION OF QUERCETIN IN PHARMACEUTICAL FORMULATIONS

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Flavonoids are a group of polyphenolic compounds widely present in the herbal world representing an important part of human diet. Quercetin, which is a flavanol, makes 70% of total daily intake of flavonoids. Because of the characteristic chemical structure, quercetin has the ability of complexing metals and antioxidative ability.

Using equimolar solution variation method it was determined that quercetin makes a complex with zinc(II)-ion in acidic environment (pH 5.25), in stoichiometric relation quercetin:zinc(II)-ion = 2:1, with absorption maximum on λmax=363 *nm*. The ability of quercetin to make complex compounds with zinc(II)-ion was used to develop simple, precise and accurate assay to determine the content of quercetin in various samples of heterogeneous composition.

The proposed indirect spectrophotometric method can selectively determine quercetin in concentrations ranging from 0.1 to 6.0 mg/L. *LOD* and *LOQ* were derived from the calibration curve and estimated as 0.03 *mg/L* and 0.1 *mg/L* respectively. Developed method is reproductive and accurate, as indicated by high value of correlation coefficient *R*=0.99996 and low value of *SD*=0.00122. Method was successfully used to determine quercetin content in dietary supplement tablets. Dietary supplements, proscribed for therapeutic and/or profilactic pruposes, usualy content quercetin combined with other flavonoids and ascorbic acid. Therefore, it was necessary to test the selectivity of proposed method.

The reliability of the method was checked out by newly developed RP-HPLC/UV method for capsules with direct determination of quercetin after separation. The good agreement between the two methods indicates the applicability of the proposed spectrophotometric method for quercetin determination in dietary supplement tablets with high reproducibility, and enables direct and simple determination without its prior extraction from samples.

In addition, the antioxidative ability of quecetin and zinc(II)-quercetin complex was determined using oxidation-reduction standardized methods *DPPH* and *FRAP*. The same samples were tested for antimicrobial activity against seven laboratory control strains of bacteria and one yeast. As a result of those tests, there are no obstacles to combine quercetin and zinc in the same formulation.

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Keywords: quercetin; complex, zinc(II)-ion, antioxidative ability, spectrophotometry.

AEC P-20

HIDRODYNAMIC CHARACTERISTICS OF ADSORBENTS WITH FIBROUS CONFIGURATION

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At different flow rates, the hydrodynamic properties of the fixed layer of fibrous adsorbent, were investigated with high content of silicon dioxide, with different fiber lengths, and varying degrees of layer density. The parameters of the layer are defined - porosity, equivalent diameter of the channel and specific geometric and usable surfaces.

Keywords: flow rate, hydrodynamic, fibrous adsorbent, channels, usable surface.

AEC P-21

DEVELOPMENT OF RECIPES BASED ON PHYTOSYNTHESIZED NANOPARTICLES TO REDUCE BIOCENOTIC STRESS IN HORTICULTURAL CROPS

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The paper presents the background and the preliminary results obtained in the project *Development of vegetal extracts and innovative phytosynthesized nanostructured mixtures with phytotherapeutic applications to reduce biocenotic stress in horticultural crops* (Research Project no. 3, part of the Complex Project *Increasing the institutional capacity of bioeconomic research for the innovative exploitation of indigenous vegetal resources in order to obtain horticultural products with high added value* - BIOHORTINOV).

The aim of the project is represented by the development of innovative recipes based on phytosynthesized nanoparticles (obtained using natural extracts of indigenous ferns species), by applying methodologies developed by our group [1-4] and their application for the protection of vineyard culture and the apple culture.

The nanoparticles obtained using fern extracts [5], analytically characterized using modern techniques (X-ray Diffraction, X-ray Fluorescence, Transmission Electron Microscopy etc.), proved to have good antimicrobial properties, especially on microorganisms responsible for the main fungal diseases that affect the vineyard culture and the apple culture (*Venturia inaequalis*, *Podosphaera leucotricha*, *Plasmopara viticola*, etc).

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Keywords: phytosynthesized nanoparticles, vineyard, apple culture, fungal diseases.

AEC P-22

SYNTHESIS AND CHARACTERIZATION OF COMPOSITES FOR THE REMOVAL OF ENDOCRINE DISRUPTING COMPOUNDS FROM WATER

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The endocrine disrupting compounds (EDC), in its most general sense, represents compounds that can led to the alteration of the functions of the endocrine system. From the EDCs, the pharmaceuticals and personal care products (PPCP) are of particular interests, as they can produce harmful effects on wildlife and human health, even at low concentration [1, 2]. The paper presents the synthesis, characterization and application of innovative composites for the removal of endocrine disrupting compounds (pharmaceutical compounds) from water.

The obtained composites were characterized using several analytical techniques (X-ray diffraction, X-ray Fluorescence, thermal analyses, transmission electron microscopy) as well as by evaluating their removal efficiency (demonstrated by using naproxen sodium, a well-known EDC [3]).

The analytical results (figure 1 presents the TEM image of the composite) proved the successful synthesis of a core-shell composite, with good thermal stability and enhanced magnetic properties [4].

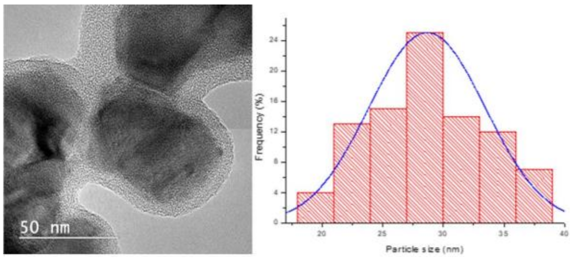

Figure 1. TEM image and particle size distribution of the composites.

In the same time, the EDC removal experiments suggests the possible application of the compounds in environmental protection applications.

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Keywords: analytical characterization, composites, endocrine disrupting compounds.

AEC P-23

USING ANTHOCYANIN PROFILES FOR THE AUTHENTICATION OF VARIOUS RED FRUITS AND PRODUCTS THEREOF

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Anthocyanins (ACNs) are a class of polyphenolic compounds, which are plant secondary metabolites that have been studied becuase of their many potential health benefits as well as because of their importance in human nutrition and food industry. Due to high costs of fruits, especially the ones that are rich in ACNs, food companies are tempted to increase profit by adulteration. For that reason, it is necessary to have methods for authentication of different fresh fruits and their procucts, e.g. fruit juices, fruit teas, fruit yogurts and jams.

The presence and pattern of specific anthocyanins can be used as markers for authentication of fruits and fruit products. Delphinidin-3-*O*-galactoside, cyanidin-3-*O*-galactoside, cyanidine-3-glucoside, delphinidine-3-*O*-arabinoside, petunidin-3-*O*-galactoside and petunidin-3-*O*-glucoside can be used as the markers for blueberries, delphinidin-3-*O*-glucoside as marker for aronia, delphinidin-3,5-diglucoside, cyanidin-3,5-diglucoside and pelargonidin-3,5-diglucoside as markers for pomegranates and cyanidin-3-*O*-glucoside-7-*O*-pentoside and peonidin-3-glucosise-pentoside as a marker for plums.

In this work HPLC/DAD/MS^n method was applied to 80 different commercial samples of fruit products from the local markets from Austria. The analytical procedure for determination of ACNs in the fruit products includes liquid-liquid extraction from the complex matrix and then separation using optimised reverse-phased HPLC-DAD-MS^n method that enables separation, identification and quantification of ACNs. 25 different anthocyanins were identified in the analysed samples and they were quantified using cyanidin 3-*O*-glucoside as external standard.

The obtained results suggest that 57 samples (25 fruit juices, 11 fruit jams, 8 dried fruits, 4 fruit yogurts, 9 fruit teas and 6 supplements) contain ACNs characteristic for the fruits from which they are derived i.e. are authentic regarding the declared fruits.

Although these methods are very powerful, this strategy should take into account the polyphenol composition variability that depends on many factors, including the cultivar, the growing region, the maturity stage, environmental conditions, processing steps and storage conditions. For that reason, we can use these compounds to verify the authenticity of fruit products, but we cannot be exact for their quantities in the processed product.

Acknowledgements: This was supported by the Macedonian Ministry of Education and Science for the bilateral project between R. Macedonia and Austria titled: “Development of analytical methods for authentication of fruit products”.

Keywords: anthocyanins, fruit products, authentication, HPLC/DAD/MSn.

AEC P-24

ANALYTICAL AND THERMODYNAMIC STUDY OF TRACE METALS IN SURFACE WATERS OF THE CENTRAL SUB-BALKAN REGION, BULGARIA

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The trace metals pollution of water basins increases as a result of the industrial, urban, agricultural and transport activities. The specific properties and reactivity of the trace metals make them of key interest, as regards cyclic geobiochemical processes.

This study covers two hot-spot industrial zones in the Central sub-Balkan region of Bulgaria: (i) *Chelopech – Zlatiza - Pirdop* with developed mining (Chelopech Mine and Elatsite Mine with copper and copper-porphyry gold-containing ores) and metallurgical (copper production plant) activities; and (ii) *Sopot – Kalofer – Gorno Sahrane* with developed machinery construction and logging industries. Three water sources were studied in each area. Their physico-chemical (temperature, pH, conductivity, dissolved oxygen and salinity) and chemical (concentrations of the major ions (Cl^-, SO_4^{2-}, K^+, Ca^{2+} and Mg^{2+}), nutrients (PO_4^{3-}, NO_2^-, NO_3^- and NH_4^+) and trace metals (Al, Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb)) characteristics were determined.

The analytical data obtained revealed that most polluted were the waters in the area of Chelopech Mine, followed by the Sopot area. Among the trace metals, Cu was found to be the most widespread pollutant, followed by Al. In all studied water stations the Cu and Al values exceeded the maximum allowed concentrations by a factor of 5-6 and 1-2.5, respectively, according to the Bulgarian regulations. The highest pollution was registered in Chelopech Mine region for Cu, Zn, Pb and Mn and in Sopot for Zn, where they exceeded the levels of allowed concentrations for waters in industrial zones. The contents of Fe, Mn, Co, Ni, Zn, Cd and Pb were below their allowed concentrations in all other studied stations. From the nutrients only the concentration of PO_4^{3-} ions exceeded the allowed one in all studied stations.

The classical ion-association model with the computer program Visual Minteq, v. 3 was employed for thermodynamic modeling. The obtained data were used for modeling of inorganic complexations, as well as for prediction of precipitation processes and calculation of chemical species distributions of the studied trace metals. More significant differences in the species distribution in the studied waters of both zones were found for Fe, Mn, Ni and Zn. Spontaneous precipitation of $Pb_5(PO_4)_3Cl$, $Fe(OH)_3$, $Al(OH)_3$ and $MnHPO_4$ was calculated, that reduced the concentration of Al, Fe and Pb by more than 90 % and that of Mn by 28 to 98 %. The combination of possible precipitation and formation of stable hydroxy-complexes of Al and Fe and carbonate and hydroxy-complexes of Cu and Pb, makes these metals not so harmful for the ecosystem. In contrary, domination of free Me^{2+} ions was calculated for Mn, Co, Ni, Zn and Cd that classified them as more harmful for the ecosystem.

Acknowledgements: This work was financially supported by the Bulgarian Ministry of Education and Science under Project DN 14-7/2017.

Keywords: surface waters; trace metals; analytical data; thermodynamic modeling.

AEC P-25

THERMODYNAMIC MODELING FOR EVALUATION OF TRACE METALS IMPACT ON THE ECOSYSTEM IN THE PROTECTED SITE PODA, BULGARIA

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The protected site PODA, Burgas, Bulgaria, is of special interest because of its importance for avian species, its proximity to a large city, and its history of human transformations. Trace metals are amongst the key environmental pollutants due to their specific properties and reactivity. Their toxic impact on the ecosystem is not only a function of their concentrations but of their chemical species as well.

In order to more effectively assess the influence of trace metals on the ecosystem in this protected area, we investigated 5 water stations and their nearby soils and aqueous soil extracts by applying two approaches - physicochemical characterization and thermodynamic modeling. The experimental data obtained for the water basins and for the aqueous soil extracts in respect of total concentration of major ions (Cl^-, SO_4^{2-}, K^+, Ca^{2+} and Mg^{2+}), nutrients (PO_4^{3-}, NO_2^-, NO_3^- and NH_4^+), trace metals (Al, Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb), dissolved organic carbon (DOC), dissolved oxygen and pH were used as input data. For calculation of trace metals' inorganic species distribution the ion-association model and for the organic species – the Stockholm Humic Model was applied. Also, the possible spontaneous precipitation was calculated in order to predict the self-cleaning potential of the studied water system. Computer program Visual Minteq, Version 3 was used. The redox processes in all cases were estimated using data for all oxidation-reduction processes that could proceed, namely O^0/O^{2-}, N^{3+}/N^{5+}, N^{3-}/N^{5+}, Co^{2+}/Co^{3+}; Cu^+/Cu^{2+}; Fe^{2+}/Fe^{3+}. The results showed that in the examined water samples the O^0/O^{2-} process dominated, the only exception being one soil extract with a high NO_3^- concentration (28 mg/l), responsible for the domination of $N^{3+}/N^{5+}$and N^{3-}/N^{5+}. We have calculated negligible amounts of Co^{3+}, Cu^+ and Fe^{2+} ions. Mn^{3+}, Mn^{6+} and Mn^{7+} ions were not considered in the calculations, since they are not stable in natural waters.

$Al(OH)_3$, $Pb_5(PO_4)_3Cl$, $MnHPO_4$, $CaCO_3$, $Ca_3(PO_4)_2$ (am) and $MgCO_3$ were calculated to precipitate spontaneously in the studied water basins, whereas in the aqueous soil extracts these precipitants, excluding $MgCO_3$, were attended by $Fe(OH)_3$, $MnCO_3$, $CdCO_3$, $NiCO_3$ and $CaSO_4.2H_2O$ in different combinations, depending on element concentrations and pH. These results revealed the self-cleaning potential of the studied waters in respect of Al, Pb, Mn and PO_4^{3-}, and for the aqueous soil extracts additionally in respect of Fe, Cd, Ni and SO_4^{2-}. Spontaneous precipitation and corresponding self-cleaning potential in respect of Co, Cu, and Zn were not calculated. Most harmful for the ecosystem are Mn, Co, and Ni, since they exist in the waters and aqueous soil extracts mainly as free Me^{2+} ions. Less significant for the ecosystem are the Al species which exist as hydroxy or organic-hydroxy complexes, as well as Fe, Cu, and Pb, for which organic and organic-hydroxy complexes were calculated as dominant. Intermediate position is taken by Zn and Cd, which, depending of DOC concentration, were calculated with a domination of free ions or of organic complexes.

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Keywords: thermodynamic modeling, chemical species, trace metals pollutions.

AEC P-26

GOLD DECORATED SILICA CORES - SYNTHESIS, CHARACTERIZATION AND EXTRACTION EFFICIENCY TOWARD Hg(II) AND METHYLHg

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Nanocomposite material, submicron silica spheres as a core, decorated with Au nanoparticles was synthesized and characterized. Micron-sized silica spheres with low polydispersity were obtained from submicrospherical silica seeds by modified seeded growth technique. Spherical silica seeds were prepared by rapid mixing of TEOS (in ethanol) with ammonia in water-ethanol solution, at constant temperature of 30 ± 1 °C, under stirring. Thereafter fifteen seeded growth steps were conducted without secondary nucleation resulting to micron-sized silica spheres. Reduction of $HAuCl_4$ by D-glucose in the presence of NaOH as a catalyst was used for green synthesis of AuNPs. The core-shell nanocomposite SiG-AuNPs was prepared after colloid mixing of both suspensions under ultrasound stirring. Extraction efficiency of SiG-AuNPs toward iHg(II) and methyl Hg was studied in model solutions containing 0.1 µg L^{-1} of both species in the presence of 0.001-0.01 mol L^{-1} HNO_3 or HCl. Results obtained showed that both Hg species are retained quantitatively on the surface of the sorbent for a relatively short time – about 30 min. The mechanism of this sorption is elucidated – most probably iHg(II) is first absorbed, than reduced and finally Au-Hg amalgam is formed. It might be suggested that as a strong catalyst AuNPs on the surface of the sorbent initially ensured demethylation of methylHg and after that the same mechanism of retention as for Hg(II) is realized. Amalgam formation predicts the way of elution – the only possibility is sorbent dissolution in aqua regia. As far as very low amounts of sorbent were used for each sorption cycle this ensures higher retention efficiency on always freshly prepared sorbent. In order to confirm the applicability of SiG-AuNPs for total Hg determination in surface waters experiments with different types of waters (tap, river, lake, sea) were carried out. The recoveries achieved varied in the range 92-96% for both Hg species.

Acknowledgements: The study was supported through bilateral agreement between Bulgarian Academy of Sciences and Macedonian Academy of Sciences and Arts.

Keywords: mercury, gold nanoparticles, SPE.

AEC P-27

IONIC LIQUID GRAFTED ON SUBMICRON SILICA SPHERES – EFFICIENT SORBENT FOR NOBLE METALS

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Determination of noble metals is important and in the same time difficult analytical task due to their low concentrations and high spectral interferences. The application of enrichment is inevitable for the most of the analyzed samples – environmental, waste materials, geological samples. Solid phase extraction is conventionally used as easy, simple and suitable for routine analytical practice procedure. Extraction efficiency of sorbent determines the selectivity, enrichment factor and sensitivity of developed analytical procedure. The goal is separation and enrichment of all noble metals if possible with high sorption capacity. In the present study new sorbent is synthesized based on 1-imidazolium grafting on the surface of submicron silica spheres. The sorbent surface is positively charged which allows quantitative sorption of chlorocomplexes of noble metals – Au, Pd, Pt, Ir, Rh. The optimal conditions e.g. concentration of HCl, sorption time, eluent type and desorption time were investigated. It was found that in the presence of relatively low HCl concentration quantitative sorption for less than 20 min is achieved for Au, Pd, Pt and Ir. The degree of sorption for Rh was in the range 50-70% for all HCl concentrations studied. Solution of thiocarbamide 0.5 mol L^{-1} in 1 mol L^{-1} was the optimal eluent ensuring quantitative elution for 15 min. The selectivity toward non noble metals was evaluated. The analytical procedure is developed for the determination of noble metals in waste materials.

Acknowledgements: The study was supported through bilateral agreement between Bulgarian Academy of Sciences and Macedonian Academy of Sciences and Arts.

Keywords: noble metals, silica spheres, ion impinted polymers.

AEC P-28

SYNTHESIS AND CHARACTERIZATION OF CATALYTIC SYSTEMS COMPOSED OF METALLIC OXIDES DEPOSITED ON Al_2O_3 WITH APPLICATIONS IN ADVANCED OXIDATION PROCESSES

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For the removal of endocrine disrupting chemicals (EDCs) from water, several strategies can be applied (such as the use of activated carbon, adsorption, catalytic ozonation, etc.), every strategy having its limitations [1]. Among the advanced oxidation treatments, the catalytic ozonation process is distinguished by its features that allow application in the depollution of a wide range of apical effluents. Catalytic ozonation is a flexible and efficient method because it can be used either by implementing it in a treatment or single process [2]. Generally, transition metal oxides have a good activity in the processes of oxidation of organic or inorganic substances present in water [3].

The present paper describes the synthesis of such catalytic systems and their characterization using several analytical techniques (X-ray diffraction, X-ray Fluorescence, thermal analyses, transmission electron microscopy, inductively coupled plasma – atomic emission spectrometry, Determination of textural features).

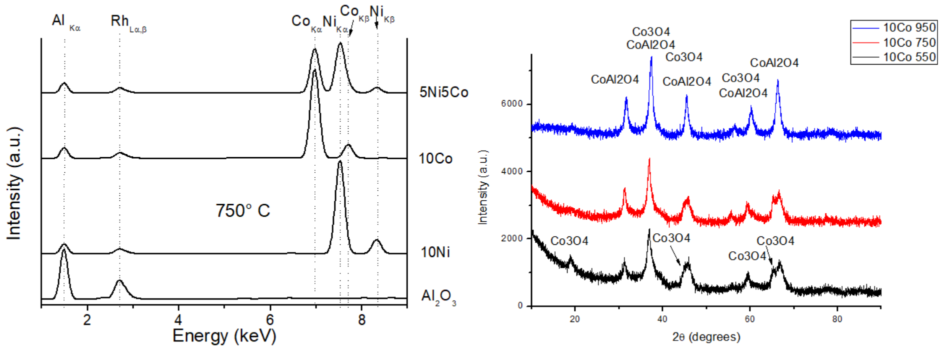

Figure 1. XRF spectra of different catalytic systems calcinated at 750°C (left) and XRD diffractograms of one of the catalytic systems calcinated at different temperatures (right)

The analytical results confirmed the synthesis of the catalytical systems, in the same time supporting their potential application in advanced oxidation processes.

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Keywords: catalytic systems; advanced oxidation processes; analytical characterization.

AEC P-29

TRANSDISCIPLINARY METHODOLOGIES FOR THE STUDY AND VALORISATION OF CULTURAL HERITAGE ARTIFACTS

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The present paper aims to present the methodologies developed in the project *Techniques for storing and capitalization the results of advanced scientific research* (SoVaReX), demonstrative scientific experiment *Transdisciplinary studies for the valorization of the national cultural heritage.* Using our previous experience in the area of cultural heritage studies [1, 2], the project aims to provide the IT&C support, presented as a computer system for the acquisition, processing, storage, modelling and analysis of advanced scientific experiments, developed by the project coordinator, IFIN-HH.

The developed methodologies (Figure 1a), combining several nuclear and associated techniques (X-ray diffraction, X-ray fluorescence, Particle induced X-ray emission, thermal analyses, FTIR, microscopy techniques, microbiological evaluation etc.), applied in the study of cultural heritage artifacts (especially metallic artifacts, historical textiles and wood artifacts) resulted in a large quantity of results deposited in the database developed by the coordinator (Figure 1b) and were subject of several published works [3, 4].

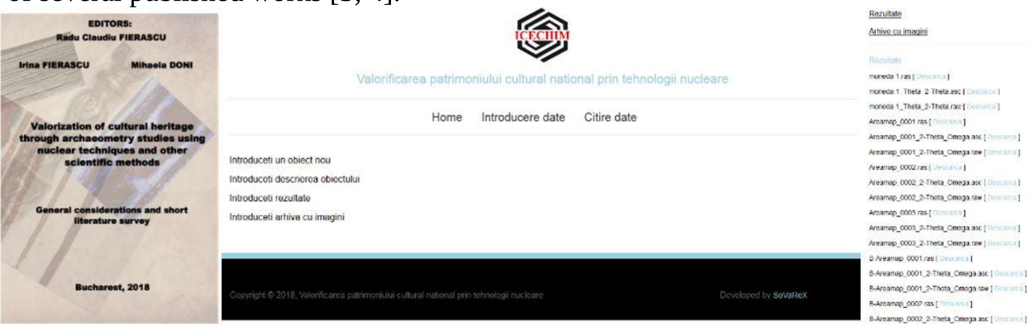

Figure 1. E-book containing the developed methodologies (a – left) and images of the database and (some) of the contained results (b – center and right)

The demonstrative experiment presented in the paper led to the validation of both the proposed methodologies and of the computer system. Supplementary information are available on the web-page of the project (http://sovarex.nipne.ro/) and of the demonstrative experiment (http://sovarex-patrimoniu.nipne.ro/).

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Keywords: analytical techniques; cultural heritage artifacts; transdisciplinary methodologies.

AEC P-30

DEVELOPMENT OF NANOMATERIALS AND NANOSTRUCTURES FOR PRESERVATION OF CULTURAL HERITAGE ARTIFACTS

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The paper presents the general objectives and preliminary results obtained in the project *Nanotechnology – an innovative approach with development of materials and techniques for safeguarding the cultural heritage* (Research Project no. 2, part of the Complex Project *Multidisciplinary complex project for monitoring, preservation, protection and promotion of the Romanian cultural heritage* - RO-CHER). Several apatitic nanomaterials with proven antimicrobial properties [1, 2] are considered for developing innovative recipes to be applied for the restoration and conservation of paper and, respectively, ceramic artifacts.

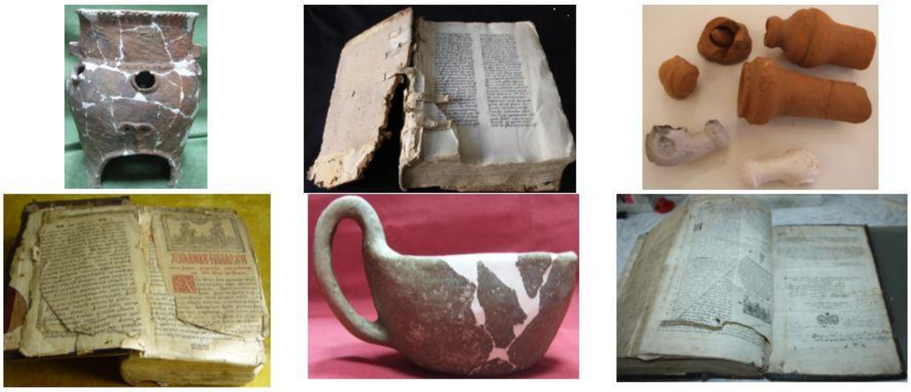

Figure 1. Some of the artifacts considered for the study.

By performing archaeometry studies on each type of artifact [3, 4], the recipe will be adapted, considering the particularities of the materials, as well as the interactions between the support material and the nanomaterials.

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Keywords: nanomaterials, paper artifacts, ceramic artifacts, preservation.

AEC P-31

SOL-GEL SYNTHESIS OF MODIFIED ZINC OXIDE NANOPARTICLES FOR METALLIC COATINGS AND THE ANTI-CORROSIVE EFFECT OF THE FINAL MATERIALS

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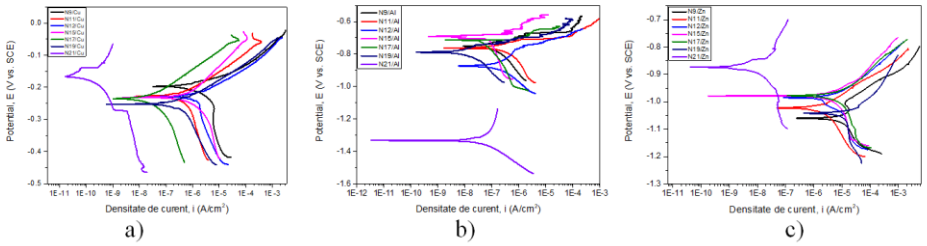
As far as corrosion science is concerned, many efforts have been taken for using materials based on silane as adhesion promoters between metallic substrates and organic coatings, used to protect against corrosion phenomena. Silane films also provide a thin but effective barrier against oxygen diffusion at the metal interface [1].

This paper presents an original contribution for obtaining low-size zinc oxide (ZnO) nanoparticles by sol-gel process, using precursors with variable organic functionality [2], to develop coating on different metallic substrates (aluminum, copper, zinc) with anticorrosive property.

Tests for determining the anticorrosive effect of metallic substrates covered with modified ZnO materials were performed by the linear polarization technique.



a) b) c)

Figure 1. Tafel curves of metallic substrates a) Cu, b) Al, c) Zn, covered with different modified ZnO materials

After analyzing all the electrochemical parameters and comparing the results for each material deposited on every metal, it can be said that the material deposited on Cu substrate, have the most electropositive values of the potential of the circuit and the potential of the corrosion.

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Keywords: sol-gel synthesis; metallic coating; corrosion resistance.

AEC P-32

FAST SIMPLE HIGH-THROUGHPUT HPLC METHOD FOR QUANTIFICATION OF NITROGLYCERIN IN RETARD TABLETS

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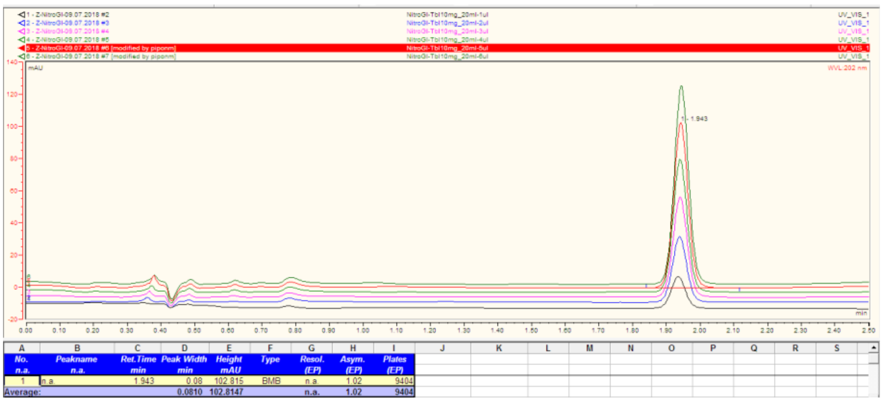
We developed fast simple HPLC method for quantification of Nitroglicerin in slow release or retard tablets. Our method employs some practical improvements considering other published chromatographic method. Including of acetonitrile in the mobile phase mixture with water and methanol, reduces run time, column backpressure and UV monitoring baseline fluctuations. These moments results in increasing sensitivity and selectivity of method. Nitroglycerin has poor UV response with unpleasant absorption spectrum appearing at less than 220nm wavelengths. We could use UV-measuring signal at 202 nm, tested and compared with columns with dimensions 250x4mm, 75mm and 50mm, filled with 5um fully porous or porous-shell C8 or C18 particles. The final concept method can be easily applied for Nitroglycerin quantification in Determination of Tablets Content, Tablets Content Uniformity and Tablets solubility in Slow Release and Retard Tablets, regarding as High-Throughput chromatographic analysis. Further investigations of method will check its applicability in early or late stage of stability indicating preferences. Method characteristics for the Nitroglycerin were compared for their applicability when 3500, 9500 and 16500 number of theoretical plates are achieved.



No. n.a.	Peakname n.a.	Ret.Time min	Peak Width min	Height mAU	Type	Resol. (EP)	Asym. (EP)	Plates (EP)
1	n.a.	1.943	0.08	102.815	BMB	n.a.	1.02	9404
Average:			0.0810	102.8147		n.a.	1.02	9404

Keywords: nitroglycerin, HPLC, UV, method, tablet.

AEC P-33

THREE DIFFERENT STRATEGIES IN DEVELOPMENT OF HPLC METHOD FOR SIMULTANEOUS DETERMINATION OF PARACETAMOL AND IBUPROFEN IN TABLETS

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We describe three different approaches in development of simultaneous quantifications of paracetamol and ibuprofen in solid dosage pharmaceutical forms. These two active pharmaceutical ingredients have quite different chemical characteristics, solubility expressed as Log P octanol water for paracetamol 0.31 and 3.97 for ibuprofen. Their difference in pKa values 4.85 for Ibuprofen and 9.5 for paracetamol, additionally complicate development of appropriate quantification HPLC method. The main problem in simultaneous determination of paracetamol and ibuprofen is significant differences in their retentions on chromatograms, resulting with enormous and excessive peak resolution. Usually is a problem to retain paracetamol longer or to elute Ibuprofen earlier, in aim to get appropriate reasonable chromatogram.

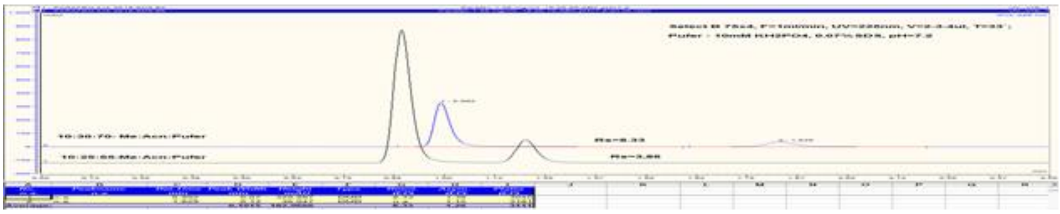
In this aim, the experimental strategies were investigated:

1. Change of organic modifiers and pH of mobile phase
2. Change of type of reversed phase sorbents to shorter alkyl chains up to cyano-propyl ligand
3. Employment of an ion-pairing agents with long alkyl chains up to dodecylsulphate

-First approach is least attractive with use of obligate neutral to weak basic pH of mobile phase, often with use of3 amino-modifiers of peak, and unnecesery huge peak resolution

-Second approach works with most UV-transparent phosphate buffers with pH range 6-7. Use of cyanopropyl chromatographic column is usually with lower number of theoretical plates for peaks, which appear slightly thicker, but with perfect retentions and resolution of Paracetamol and Ibuprofen, and shorter run time

-Third and most attractive approach for us was addition of 0.07% w/v sodium dodecyl sulphate in 10mM phosphate buffer with 10% methanol and 20% acetonitrile, which generates chromatogram within less than 2 minutes with R resolution about 3.5 using column of 50-75mm in length with 5um particles generating about 2300 number of theoretical plates.



Keywords: paracetamol, ibuprofen, HPLC, UV, method.

AEC P-34

PREPARATION OF THE FATTY ACID DERIVATIVES OF CASTOR OIL BY METHANOLYSIS

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Fatty acid derivatives represent an important starting material for producing a number of oleo chemicals, such as soap, fatty alcohols, alpha sulfomethyl esters, sucrose esters, detergents, etc. in pharmaceutical, cosmetic and chemical industry. Also, they are raw chemical substances in forms and different formulations of pharmaceutical and cosmetic products for preparation of surfactants, emulsifiers, softeners, and lubricants. The aim of this work was to prepare fatty acid derivatives of castor oil by methanolysis using alkaline catalyst sodium hydroxide. Synthesis and reaction were carried out with excess of anhydrous methanol, at room temperature under reflux condition, during four hours, in two parallels. Excess of methanol was removed by neutralization with dilute sulphuric acid, while obtained mixture methyl esters and glycerol separated and purified by fractional distillation. Physical and chemical properties for fatty acid methyl esters of castor oil was determine according to standard analytical methods for fat and oils. Our results of preparation of fatty acid methyl derivatives of castor oil by methanolysis and their analysis showcased its potential and relevance in cosmetic and pharmaceutical application. It can be used as raw material in different formulations, as well as for production of valuable co-products, such as glycerol.

Keywords: fatty acid derivatives, castor oil, methanolysis.

AEC P-35

DETERMINATION OF TOTAL IRON CONTENT IN SELECTED HERBAL TEA PRODUCTS

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The tea of different herbs the most perfered drink after water worldwide. In Bosnia and Herzegovina popular are peppermint (*Mentha piperita* L.), sage (*Salvia officinalis* L.), chamomile (*Matricaria chamomila* L.), tea - black and green (*Camellia sinensis* L.) herbal teas as well as rose hip (*Rosa canina* L.) fruit tea. These herbal teas were consumed for medicinal purposes and for maintaining good health. Iron is an essential element for plant growth and development while in human metabolism, iron is an important component of proteins involved in oxygen transport as well to normal human physiology. The aim of this study was to determine of the total content of iron in selected herb tea products from different brand manufactures, available in a local market in Sarajevo. The preparation of the samples was done in triplicate by dry digestion in furnace (at 500^0C and during 4 hours), while levels of iron were analysed by spectrophotometry. The concentrations of iron were ranged from 320.8, 406.3, 169.5, 168.4 and 112.6 to 139.8 mg Fe/kg for peppermint, sage, chamomile, tea (black and green) and rose hip, respectively. All tested herbal tea products showed high levels of iron especially in sage and peppermint that can supply enough daily iron recommendations in humans. The used spectrophotometric method is simple and sensitive method for the determination of very low concentrations of iron and total iron content in herbal materials.

Keywords: iron, herbal teas, dry digestion.

AEC P-36

IDENTIFICATION OF BULGARIAN HONEYDEW HONEYS AND MONOFLORAL HONEYS

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Honey is a natural sweet substance produced from bees (*Apis Mellifera*) and in the recent years honey acquires wider significance in the light of healthy human diet. According to the origin of the plant honey is classified as a blossom or honeydew honey. Blossom honey is produced from the nectar of flowers of blossoming plants, whether honeydew honey is produced from the secretions of plants or from the excretions on plants of plant-sucking insects. On the other side blossom honey is divided of monofloral (obtained mainly from nectar of one plant species such as black locust, lime, sunflower, thistle, rape, lavender, etc.) and polyfloral (obtained from different types of floral nectar), whether honeydew honey is divided to coniferous (obtained mainly from coniferous plants – pine, fir) and oak (obtained mainly from oak plants). The constituents of honey (carbohydrates, minerals, enzymes, amino acids, pigments, variable amounts of sugar-tolerant yeasts, pollen, traces of vitamins, organic acids and wax) depends on different factors during honey maturation. Some of them are added by the bees, and some are derived from the plants. However, it is assumed that honey composition from the same floral source can also vary due to seasonal climatic variations or to a different geographic origin. In case of doubt or fraud, there are no standardized protocols available that can discriminate or determine the botanical (floral or vegetable) and geographical (regional or territorial) origin of the honey. The aim of the present study is to (i) characterize honeydew honey (coniferous and oak) and monofloral honey samples (black locust, lime, sunflower, thistle, rape) produced in Bulgaria with guaranteed geographical and botanical origin in the point of view of physicochemical parameters (such as color, water content, specific rotation, electrical conductivity, pH, total acidity, hydroxymethylfurfural, diastase activity, proline content) and chemical elements content (such as Al, B, Ba, Ca, Cd, Fe, K, Mg, Mn, Na, P, Pb, Sr, Zn), and (ii) to determine appropriate descriptors for differentiation and botanical origin determination of analyzed honey samples.

Acknowledgements: The authors are grateful for the financial support by Bulgarian National Science Fund Grant № DM 19/1 and Science Fund in Sofia University "St. Kl. Ohridsky" Grant № 80-10-221.

Keywords: honeydew honey, monofloral honey, physico-chemical parameters, elemental composition.

AEC P-37

COMPARISON OF THE ADSORPTION PROPERTIES OF *Mentha spicata* L. AND *Ruta graveolens* L. WITH RESPECT TO THEIR USE AS BIOSORBENTS FOR Cu^{2+} AND Cd^{2+} IONS

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The release of toxic metals into the environment is a serious worldwide problem, caused by industrial activities such as mining and metal processing. Numerous attempts have been made to treat wastewaters containing toxic metals by conventional technologies. Biosorption has recently attracted growing interest as it is a new method involving the removal of toxic metals from contaminated waters, based on metal binding capacities of various biological materials. Cadmium is a very toxic element affecting the environment and humans. Copper is an essential element, but it is also hazardous at high concentrations. Both ions are transferred to humans via the food chain therefore to eliminate them from aqueous media is an important ecological task.

In the present study plant materials based on *Mentha spicata L.* (denoted as MS) and *Ruta graveolens L.* (denoted as RG) were compared concerning their adsorption properties towards Cu^{2+} and Cd^{2+} ions. Batch experiments were performed to evaluate the effect of contact time, acidity and initial metal concentration on Cu^{2+} and Cd^{2+} removal from aqueous solutions. Pseudo-first order, pseudo-second order and intraparticle diffusion models were used to analyse kinetic data. Pseudo-second order model provide the best fit to the experimental data. Equilibrium data were fitted to linear Langmuir and Freundlich models. It was established that Freundlich isotherms most adequately describe the adsorption process for both ions. Maximum adsorption capacities were calculated and it is concluded that both plant materials show better adsorption properties towards Cu^{2+} ions as compared to Cd^{2+} ions. Nevertheless, our previous investigations[1] and the obtained results in the present study show that MS and RG could be used as effective biosorbents for the removal of copper and cadmium ions from aqueous media.

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Acknowledgements: The authors are grateful for the financial support to the Program for supporting young scientists and PhD students from the BAS – 2017 (Project No DFNP-17-35/25.07.2017).

Keywords: biosorption of Cu^{2+}, biosorption of Cd^{2+}, water purification.

AEC P-38

HPLC METHOD DEVELOPMENT FOR DETERMINATION OF ACTIVE INGREDIENT IN PESTICIDE FORMULATIONS MONOSAN HERBI AND DMA-6

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Monosan herbi and DMA-6 are pesticide formulations in the form of a liquid solution concentrate (SL) registered in the Republic of Macedonia, in which the active substance is 2,4-D ((2,4-dichlorophenoxy)acetic acid).

A new, fast and simple high-performance liquid chromatography (HPLC) method for determination of an active ingredient 2,4-D in the pesticide formulations Monosan herbi and DMA-6 has been developed. The development of a HPLC method was performed on a Purospher STAR RP-8e (30 mm x 4 mm; 3 µm) analytical column and ultraviolet-diode array detection (UV-DAD). The best results with symmetrical peak shape and good index purity of the analyte were obtained using acetonitrile:water (45:55, *V*/*V*) as the mobile phase with flow rate of 1 mL/min, column temperature at 25 °C and UV detection at 220 nm. The specificity, selectivity, linearity, precision, accuracy, limit of detection (LOD) and quantification (LOQ) were tested for the method validation according to the CIPAC (Collaborative International Pesticides Analytical Council) guidelines and all tested parameters were found within acceptance criteria. The method had a good linear relationship in the range of 1.82 - 14.59 µg/mL ($R^2 = 0.9998$). The intra- and inter-day precisions were evaluated for the retention time, peak area and peak height. Under the stipulated conditions, the calculated values for recovery were between 98 % - 102 %, with relative standard deviations below 2 %. The developed method was successfully applied for qualitative and quantitative determination of an active ingredient 2,4-D in the pesticide formulations Monosan herbi and DMA- 6, and the obtained values for the content of an active component corresponded to the values declared by the manufacturers. The obtained results indicated that the proposed method is characterized by excellent linearity, precision and accuracy, and can be used for routine analysis of the active ingredient 2,4-D in the preparations Monosan herbi and DMA- 6 following the CIPAC rules.

Keywords: HPLC, method development, active ingredient, Monosan herbi, DMA-6.

AEC P-39

HPLC METHOD DEVELOPMENT FOR DETERMINATION OF SOME PESTICIDE RESIDUES IN WATER SAMPLES

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This study presents a development of a new high-performance liquid chromatography (HPLC) method with ultraviolet-diode array detection (UV-DAD) for simultaneous determination of 2,4-D, atrazine, malathion, fenitrothion and parathion residues in water samples. Separation and quantitative determination of the analytes were carried out using a LiChrospher 60 RP-select B (250 x 4 mm, 5 µm) analytical column, under the isocratic elution with mobile phase consisted of acetonitrile/water (60/40, *V/V*), flow rate of 1 mL/min, constant column temperature at 25 ˚C and UV-detection at 220 nm and 270 nm. A solid-phase extraction using C-18 columns was carried out for enrichment and clean-up of target components. The developed method was validated by testing specificity, selectivity, linearity, precision, accuracy, limit of detection (LOD) and quantification (LOQ) according to European Commission guidelines for pesticide residue analytical methods, and all performance characteristics were found within acceptance criteria. The method had a good linear relationship in the range of 0.1 – 0.5 µg/L for all selected pesticides. The precision was evaluated for the retention times and peak areas of analytes and the obtained values for relative standard deviations (RSD) were 0.12 % - 0.22 % and 0.61 % - 5.85 %, respectively. Under the established conditions, the recoveries were between 92.53 % - 111.67 %, with relative standard deviations 0.22 % - 13.94 % for all analytes. The developed method was successfully applied for simultaneous determination of the examined pesticides in different water samples (tap water, non-carbonated water, purchased from Macedonian supermarkets and water from the river Vardar). The obtained results showed that analyzed water samples did not contain detectable residues of investigated pesticides.

Keywords: HPLC, method development, pesticide residues, water samples.

AEC P-40

SIMPLE ELECTROANALYTICAL METHODS FOR SUNSET YELLOW ARTIFICIAL DYE (E-110) DETERMINATION IN FOOD

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A possibility of using voltammetry at electrochemically activated glassy carbon electrode for the direct determination of artificial azo-dye, Sunset Yellow, is demonstrated. The Sunset Yellow, known also as E110, may have detrimental effects on living organisms. Thus, their content in food must be strictly controlled, especially in candies, beverages and soft drinks. Despite other analytical methods for determination of azo-dyes, the electroanalytical methods, especially voltammetric methods, offer many other advantages besides high sensitivity, selectivity and reproducibility. [1]

The electrochemical behaviour of the Sunset Yellow is studied by cyclic voltammetry using the activated glassy carbon electrode. It is shown that the signal of electrochemical reduction and oxidation of Sunset Yellow is the most pronounced in a neutral medium at pH 7.0 in 0.1 mol dm^{-3} KNO_3. The dependence of the electrochemical current of the dye on its concentration (potential of –0.688 V for reduction and 0.780 for oxidation of Sunset Yellow) is linear over a wide range (90 to 13500 mg/L with the determination limit 90.4 mg/L and detection limit 45.2 mg/L. A procedure for quantifying the dye in several food products and drinks is proposed.

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Keywords: azo–dyes, sunset yellow, voltammetric methods, in food analysis.

AEC P-41

ELECTROCHEMICAL BEHAVIOR OF MIXED SILVER-COPPER SULFIDE TOWARD H_2O_2: ANALYTICAL APPLICABILITY FOR BIOSENSING SYSTEMS

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Comparative study of electrochemical behaviors of mixed silver-copper sulfides and silver sulfide has been made in order to investigate its analytical applicability as mediators in biosensing systems (containing oxidases or peroxidases). X-ray diffractometry (XRD) of prepared powder of mixed silver-copper sulfide revealed that beside ternary sulfides (AgCuS and $Ag_{1.2}Cu_{0.8}S$) also metallic silver can be found. The electrocatalytical activities of sulfides were evaluated towards the detection of hydrogen peroxide (H_2O_2) at various pH values. Cyclic voltammetry was carried out to determine the exact reduction (0 V) and oxidation (0.25 V) potentials for the electrochemical reaction of H_2O_2 on carbon paste electrode modified with mixed silver-copper sulfide or silver sulfide. Tentative electrochemical reaction mechanisms for observed phenomenon are proposed. The amperometric studies revealed that the mixed copper-silver sulfide modified carbon paste electrode performed well by attaining a wide linear response range toward H_2O_2 from 1 μM to 3 mM with detection limit 0.14 μM and the sensitivity of 350 μA mM^{-1}. In addition, good selectivity, rapid and stable response towards H_2O_2 is obtained. Obtained results suggest promising paths for selective and sensitive application of sulfide modified electrode in biosensing system.

Keywords: hydrogen peroxide, silver-copper sulfide, carbon paste, electroanalytical, biosensing.

AEC P-42

DETERMINATION OF MINERAL NUTRIENTS IN RAW NUTS AND SEEDS FROM THE MARKETS IN SKOPJE

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Nuts and seeds provide healthy mono- and polyunsaturated plant oils as well as protein. Legumes, which include beans, are filling and also contain lean protein. All of these foods are packed with vitamins and minerals. Nuts and seeds are excellent sources of antioxidants such as vitamin E and plant sterols and soluble fibers. They are also abundant in minerals. The aim of this work includes the investigation for establishing the levels of mineral nutrients as well as some toxic elements in nuts, seeds and legumes, which can be found on the markets in Skopje on a daily base. This study was conducted to raw, unprocessed nuts, seeds and legumes (both shelled and unshelled) excluding mixed, roasted or salted products. In total, 38 products from different suppliers were analyzed, with the number of samples per nut/seed variety reflecting the availability of unprocessed products. Variety of nuts (almonds, hazelnuts, walnuts, cashew nut, pistachios and peanut) and for the seeds (quinoa, chia seed, beans, lentil and rice) were analyzed. The terms of nuts and seeds used in this investigation are with their trivial meaning, not in the botanical sense. This investigation includes samples from tree different markets in Skopje. Different samples of nuts, seed and legumes were grounded in to a fine powder and processed, digested with microwave system and then analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). It was found that the samples of chia seeds and almonds are especially high in calcium (range from 8324–9770 mg/kg and 2338–6220 mg/kg, respectively) and magnesium (range from 3758–5841 mg/kg, 2639–5572 mg/kg, respectively), while cashew nut are reach with cooper (range from 34.9–45.3 mg/kg). All nuts and seeds are rich in zinc. From these studies it has been found that in this type of food, there is no high content of toxic elements above the permitted values according to the national regulation, and they are safe to be consumed.

Keywords: mineral nutrients, toxic elements, nuts, seeds, markets, Skopje.

AEC P-43

CHARACTERIZATION OF MULTI-ELEMENTS CONTENT AND ISOTOPES RATIO PROFILES FOR VARIOUS PLANT FOOD DUE TO THE HISTORICAL AND MODERN METAL POLLUTION

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Determination of the geographical origin of food and beverages has been a growing issue over the past decade for all countries around the world, mostly because of the concern of consumers about the authenticity of the food that they eat. An increasing number of research articles in the past years have investigated the elemental composition and the isotope ratios as indicators to determine the origin of food and beverages.

The present investigation summarized the data for application of validated method including multi-element and multi-isotope chemical characterization and the statistical tools in order to be used for determination of the geographical origin of food and beverages. Comparative analysis (between samples collected from R. Macedonia vs. samples collected from P. R. China) were used for improving the large-scale application of the implemented proposed method. Inductively coupled plasma with mass spectrometry (quadropole based) was used for the isotopic measurements of the following total 69 elements: Ag, As, Al, Au, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In,Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, P,Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Ti, Th, Tl, Tm, V, W, Y, Yb, Zn and Zr.

Keywords: Multi-element characterization, lead isotope ratios, plant food, ICP-MS-Q.

AEC P-44

NEW ADSORBENT BASED ON CARP SCALES MODIFIED WITH CERIUM NANOPARTICLES FOR THE REMOVAL OF ARSENIC FROM WATER

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The possibility of using porous carp fish scales (Cyprinus carpio) modified with cerium for the removal of As(V) ion from aqueous solution was investigated in this study. For the first time it is reported here that fish scales can be an excellent raw material for synthesizing porous cerium supported fish scales for As(V) ion adsorption. Because of the material availability in large quantity, at the moment, the scales are considered only as a bio waste [1], and the development of the technology for the hazardous material removal from water provide multiple contribution to environmental protection. A novel, low cost adsorbent, cerium supported on carp fish scales (Cyprinus carpio) (CeO_2-FSC), has been synthesized to remove As(V) ions from water. The adsorbent synthesis consisted of chemical and thermal treatment of raw material in order to convert the fish scales into the porous fish scales doped with cerium nanoparticles. By changing the reaction conditions, the porosity and the content of the CeO_2 nanoparticles can be controlled in synthesized porous adsorbents. The optimization of the initial amount of $CeCl_3$ ratio and the carbonization temperature of the cerium nanoparticles doped adsorbent was performed with the intent to obtain a high performance adsorbent used to remove arsenate ions from water. Optimization of the reaction parameters was completed using the *response surface methodology* (RSM) where the output is the adsorbent capacity. A highly efficient material (CeO_2-FSC) with a capacity of 78.12 mg g^{-1} (Langmuir isothermal model) was obtained to remove arsenate ions from the drinking water. The adsorption studies were conducted as a function of pH, contact time, adsorbent mass and temperature. The best adsorption of arsenate ions was achieved for pH between 4.0 and 6.0. The adsorption data for arsenate at 25, 35 and 45 °C are fitted to Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin isotherm models [2]. Experimental data were used to model adsorption kinetics using pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion kinetic models. The results showed that the adsorption of arsenate ions onto CeO_2-FSC followed the pseudo-second-order kinetic model and Freundlich isotherm models. Thermodynamic parameters, including the Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) changes, indicated that the present adsorption process was feasible, spontaneous and endothermic in the temperature range of 25-45 °C.

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Keywords: arsenate, adsorption isotherms, drinking water, carp scale, CeO_2 nanoparticles.

AEC P-45

SYSTEMATIC EVALUATION OF THE DEGRADATION OF METHYL ORANGE BY FENTON PROCESS AT A WIDE RANGE OF CONCENTRATIONS OF H_2O_2 AND Fe^{2+}

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Fenton process is a chemical method for organic pollutants destruction present in waters [1]. The so called Fenton’s reagent is a mixture of hydrogen peroxide H_2O_2 and iron II ions Fe^{2+} which react at pH 3 to give hydroxyl radicals $^{\bullet}OH$, a very powerful oxidizing agent. Then $^{\bullet}OH$ oxidizes organic pollutants present in the solution [2]. The first attack $^{\bullet}OH$ leads to the transformation of organic pollutants to fragments which have different chemical properties than the initial molecule, so it is sad that the molecule has been degraded. But hydroxyl radicals permanently attack any organic fragment created in the solution by degradation, until they are transformed to CO_2 and H_2O – molecules that are not harmful for the environment (except CO_2 greenhouse effect).

Clearly, the concentrations of H_2O_2 and Fe^{2+} will have a great effect on the rate of hydroxyl radicals generation, whereby on organics degradation. We have studied the degradation efficiency of methyl orange (MTO) over a wide range of H_2O_2 and Fe^{2+} concentrations, with the aim of obtaining more information on the influence of H_2O_2 and Fe^{2+} on the process. It has been done starting with 0.04 mM Fe^{2+} and altering H_2O_2 form 0.04 mM … to 1.28 mM. The concentration of MTO during the degradation reaction was measured by UV-Vis spectrophotometry. The plots c = f(t) showed that at low Fenton’s reagent concentration the efficiency of methyl orange degradation was low as one expects, and it increased for higher concentration. The degradation rate of methyl orange was always quicker at the beginning, then it attained a plateau where the degradation was very slow or did not continue any further. At 0.64mM and 1.28 mM (for both H_2O_2 and Fe^{2+}) the oxidation of MTO was instant but after 10 minutes (0.64 mM) or 3 minutes (1.28 mM) the absorbance of the solution increased instead of decreasing because of the precipitation of iron II. Also when iron II was at 0.64 mM, the increase of H_2O_2 concentration over 0.16 mM had almost no effect.

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Keywords: Fenton’s reagent, methyl orange, degradation.

AEC P-46

DEGRADATION OF METHYL VIOLET, METHYL BLUE, AND METHYL RED BY FENTON PROCESS

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The amount of wastewater is increasing considerably every day. Therefore many cleaning plants have been built in which biological, physical and chemical methods are being applied for removing pollutants from water. The Fenton process is a chemical destructive method for the elimination of organic pollutants from water [1]. It is part of the group of methods for the destruction of pollutants, which are called advanced oxidation processes. It is a mixture of H_2O_2 and Fe^{2+} which gives hydroxyl radicals $^{\bullet}OH$ a very strong oxidant which oxidizes organic pollutants in water either by transforming them in less harmful byproducts and by mineralizing them [2]. The whole process is performed at pH 3, which is the optimal value for the Fenton process.

Here we have studied the efficiency of degradation of methyl indicators using the Fenton process with different Fenton’s reagent concentration and at different pH values. Methyl indicators are widely used in laboratories, so they are expected to be present in sewage effluents and after they reach the discharge point they enter in water streams becoming part of many other chemical pollutants.

To study the efficacy of the degradation of methyl indicators, 150 ml solution of 0.01 mM concentration of the three types of methyl indicators (methyl violet, methyl blue and methyl red) were prepared, and the pH was regulated to 3 with 0.1 M sulfuric acid, then Fenton Reactive ($H_2O_2 + Fe^{2+}$) is added. At that moment, methylindicator oxidation from hydroxyl radicals began. During the reaction time, samples were taken from the system and analyzed by UV-Vis spectrophotometer in order to monitor the degree of oxidation of the methyl indicators. From the experiments it has been found that the increase of H_2O_2 and Fe^{2+} concentrations increases the rate of organic compound degradation. This is expected because more hydroxyl radicals are produced and consequently more methyl indicators molecules oxidized. When pH was changed from the optimal value, and particularly when it was set at values over 3 (4 and 5) the degradation rate lowered strongly.

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[2] Brillas, E.; Sirés, I.; Oturan, M.A. Electro-Fenton process and related electrochemical technologies based on Fenton’s reaction chemistry, *Chem. Rev*. **2009**, 109, 6570-6631.

Keywords: Fenton process, hydroxyl radicals, methylindicator, degradation.

AEC P-47

THE INFLUENCE OF THE CHEMICAL NATURE OF ORGANIC COMPOUNDS ON THE EFFICIENCY OF THEIR DEGRADATION BY FENTON PROCESS

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The Fenton process is part of the Advanced Oxidation Processes (AOP) group. These processes are based on an oxidative reagent which is able to degrade the targeted organic pollutants in water media, either by complete elimination or by reducing their environmental harmfulness [1]. The main feature of Fenton processes is the use of hydroxyl radicals ($^•OH$) for the degradation of organic molecules that do not undergo biodegradation. The Fenton process is based on the catalytic generation of hydroxyl radicals ($^•OH$) from hydrogen peroxide (H_2O_2) by Fe^{2+} ions according to the reaction (1) [2]:

$H_2O_2 + Fe^{2+} \rightarrow OH^- + {}^•OH + Fe^{3+}$ (1)

${}^•OH$ + pollutant → fragments → → → $CO_2 + H_2O$ + inorganic ions (2)

This study was conducted with the purpose to evaluate the effect of chemical nature of organic compounds on the efficiency of the Fenton process. Four compounds has been studied, namely; ethylenediaminetetraacetic acid (EDTA), Ni-DMG complex, dinitrophenol and methyl-orange. The degradation process was monitored by an UV-VIS spectrophotometer and plots $c = f(t)$ were constructed in order to see the quantity of the compound degraded. The measurements were carried out at ambient temperature and the observation of the process was done during 40 minutes and in the presence of various concentrations of Fe^{2+} ions and hydrogen peroxide.

The results showed different reaction rate for each substance. The EDTA could not be degraded by the Fenton’s process, probably as a result of complex formation between EDTA and Fe^{2+}. This way there was no $^•OH$ generated in the solution and the Fenton reaction was inhibited. The Ni-DMG complex was not degraded either. This might have happened because of the substitution of Ni^{2+} in the complex by the Fe^{2+} ions. Dinitrophenol UV-Vis spectrum changed during time. The beginning spectrum has given two peaks: one in λ=296 nm and the other in λ=216 nm. During the time, the first peak which is the peak of absorption of the molecule has diminished, indicating degradation of the molecule. And finally methyl orange was easily degraded as $c = f(t)$ curves show.

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Keywords: Fenton process, EDTA, Ni-DMG, dinitrophenol, degradation.

AEC P-48

DEGRADATION OF TEXTILE DYE REACTIVE ORANGE 16 BY UV-ACTIVATED PEROXYDISULFATE PROCESS IN CONTINIOUS PHOTOREACTOR

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Among thousands of synthetic dyes used in the textile industry, azo dyes constitute the largest and the most important class of commercial dyes. The main adverse effects of dyes in the environment are their inhibitory effect on aquatic photosynthesis, ability to deplete dissolved oxygen and toxicity to the flora, fauna and humans [1]. Sulfate radicals-based advanced oxidation processes (SR-AOPs) are promising technologies for removal of organic pollutants from wastewaters [2]. In comparison to hydroxyl radical, sulfate radical ($SO_4^{-\bullet}$) posses equal or even higher redox potencial (2.5-3.1 V), higher selectivity and longer half-life [3]. Peroxydisulfate (PS, $S_2O_8^{2-}$) is the preferred reagent, as a source of sulfate radicals in laboratory studies, because it is quite cheap, highly stable and easily soluble [4].

The aim of this work was to examine whether it is possible to effectively remove textile dye C.I. Reactive Orange 16 (RO16) from water, in a continuous photoreactor, by means of sulfate radicals. Peroxydisulfate was used as a source of sulfate radicals, and was activated by UVC light (254 nm). Concentration of textile dye was followed at 492 nm by a UV-Vis spectrophotometer. The applied process seems to be suitable for complete decolorisation of RO16 dye (50 mg/L) under optimal operational conditions. Removal efficiency of RO16 dye was sensitive to the operational parameters, such as initial concentration of $S_2O_8^{2-}$, initial dye concentration, light intensity, initial pH value and flow rate. The rate of decolorisation was accelerated with increasing in peroxydisulfate concentration and intensity of UV light. Decolorisation is more efficient in acid medium in comparison with neutral and alkaline medium. Decreasing in flow rate leads to the increase of residence time in reactor, which had positive influence on removal efficiency of RO16 dye.

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Acknowledgments: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project TR34008).

Keywords: sulfate radicals, azo dyes, decolorisation.

AEC P-49

REMOVAL OF RADIOTOXIC ELEMENTS (Co and Sr) FROM CONTAMINATED WATER USING ENVIRONMENTALLY COMPATIBLE MAGNETIC NANOMATERIALS

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Radionuclides in water present a health hazard to organisms. In addition to natural sources, the main anthropogenic sources of radiotoxic elements are nuclear power reactors, laboratories working with radioactive materials and medical waste containing radionuclides [1]. Effective remediation of polluted environment is a priority in eastern as well as in western countries, but the cost of contaminated water remediation is extremely high. As a result, scientists are intensively trying to develop new technologies with lower costs of waste remediation to meet the regulatory standards. Several methods based on the extraction were developed and application of biopolymers such as humic acids as adsorbents and complexing agent is a topic of most intensive research [2, 3].

In this work, we describe the synthesis of structurally stable hybrid nanomaterials based on surface-modified magnetite (magnetite, Fe_3O_4) with humic substances. Nanoscale Fe_3O_4 was synthesized using a modern microwave-hydrothermal method. Properties of materials adsorption, i.e. efficiency of radionuclide removal was tested according to standard adsorption protocols and models. In our work, for the safety reasons, a model system with non-radioactive solutions of Co and Sr was used. Adsorption efficiency of Co and Sr were measured by an analytical technique with inductively coupled plasma optical emission spectrometry (ICP-OES).

The results have shown that Fe_3O_4 nanocrystals are excellent cobalt sorbents, if the cobalt solution is alkaline (pH 10 or 11) and if the concentration of nanocrystals is at least 500 mg/L. The adsorption is effective in both real samples, ie. in tap water from the Belgrade and in salt water. However, the coating of humic acid gives the reduction of the sorption power of the nanocrystals. It is shown that optimal conditions for adsorption of cobalt are not the same for adsorption of strontium. If the method of adsorption of both metals is applied at the same time, appropriate conditions must be found that depend on the pH, temperature, type of adsorbent, etc. The materials used in this work as sorbents are cheap and not toxic.

The obtained nanomaterials have high and fast efficiency and adsorption capacity of cobalt from contaminated water, while their magnetic nature provides their efficient and inexpensive separation with external magnets after the remediation process.

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Keywords: radionuclides, remediation, magnetic nanoparticles, humic acid, wastewater, adsorption.

AEC P-50

APPLICATION OF LIQUID CHROMATOGRAPHY COMBINED WITH LOW-FIELD DRIFT TUBE ION MOBILITY TIME-OF-FLIGHT MASS SPECTROMETRY (HPLC×IM-TOFMS) FOR RED WINE FINGERPRINTING

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Phenolic compounds are important quality components in red wine affecting the taste of bitterness and astringency, the color and long wine stability and aging. In this study, a rapid and sensitive analytical technique was used for detailed phenolics fingerprinting of 42 Macedonian red wines produced from different wine regions. Analyses were performed using high performance liquid chromatography in combination with low-field drift tube ion mobility time-of-flight mass spectrometry (HPLC×IMS-TOFMS). The reliability of $^{DT}CCS_{N2}$ values, based on consensus values from a standardized and reproducible workflow, was evaluated as an identification point for wine metabolomics. Using appropriate software tools for alignment and statistical evaluation, a full dataset for each wine was obtained, including retention time, accurate mass, fragment spectra and $^{DT}CCS_{N2}$. Putative compounds were further assessed by assignment of in-source and post-drift mass fragments aligned according to retention time, drift time, and accurate mass. Up to seven identification points for a single compound can be generated when data from both positive and negative mode measurements are combined. The correlation between abundance across the two ionization modes was found to be very good in many examples with correlation coefficients (R^2) values of 0.63-0.97 for eleven putative metabolites in Vranec wines, and 0.70-0.99 for nine putative metabolites in Pinot Noir.

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Keywords: wine phenolics fingerprinting, HPLC×IMS-TOFMS.

AEC P-51

DETERMINATION OF AROMA COMPOUNDS IN VRANEC WINES PRODUCED WITH DIFFERENT OENOLOGICAL PRACTICES

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Aroma compounds are vital to wine quality, determining their odour and varietal characteristics. Their concentration in wine depends on grape variety, light intensity, soil, maceration, fermentation temperature, etc. This study is focused on the determination of volatile compounds in Vranec wines, applying headspace solid phase microextraction (HS-SPME) method for sample preparation, coupled to GC-MS technique [1]. Vranec wines were produced with different vinification techniques, applying maceration time of 4, 7, 14 and 30 days, in the presence of enzyme and oak chips during fermentation, in order to determine the influence of vinification conditions on the aroma profile. A total of 63 aroma compounds were identified and quantified in the wines, belonging to different volatile families: esters, alcohols, fatty acids, aldehydes, ketones and sulphur compounds. The results showed that maceration time influenced the relative amount of volatile compounds, leading to increased content from the fourth to the seventh day. The presence of oak chips during fermentation enhanced the formation of aroma compounds, such as phenyl-ethyl alcohol, isobutyl alcohol, propanoic acid ethyl ester, butanoic acid ethyl ester, pentatonic acid ethyl ester and hexanoic acid ethyl ester. No significant effect of the enzyme on the volatiles in Vranec wines was noticed.

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Acknowledgments: This work was supported by a grant from the CEEPUS, CII-HU- 0010-03-0809 Network which is acknowledged.

Keywords: wine aroma, maceration, oak chips, enzyme, HS-SPME-GC-MS.

AEC P-52

THE EXAMINATION OF POTENTIAL FUNGICIDAL ACTIVITY ETHYL-3-(TRIFLUOROMETHYL)-1H-PYRAZOLE-4-CARBOXYLATE AND ETHYL-1-(4-NITROPHENYL)-5-(TRIFLUOROMETHYL)-1H-PYRAZOLE-4-CARBOXYLATE ON FUNGUS *Botryosphaeria dothidea* UNDER LABORATORY CONDITIONS

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Pyrazole based compounds and their transition metal complexes have a wide variety of applications in diverse fields ranging from agriculture to medicine [1]. In this paper we analyse influence of pyrazole derivatives Ethyl-3-(trifluoromethyl)-1H-pyrazole-4-carboxylate and Ethyl-1-(4-nitrophenyl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate on the inhibition of mycelium of pathogenic fungus *Botryosphaeria dothidea.* This fungus causes severe fruit rot of olives and it can be spread to the entire olive-grove. The last years, in Montenegro, fruit rotting caused extensive damage to olive trees [2].

The fungicidal activity of both compounds, in five different concentrations, ranged from 0.12 to 0.0075%, was tested for the fungus *B. dothidea* in laboratory conditions on PDA nutrient medium. Obtained results were compared with the commercial fungicide (pyraclostrobin and metiram). Both examined compounds showed a significant inhibitory effect on *B. dothidea* compared with the control.

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Keywords: pyrazole derivatives, fungicidal activity, *Botryosphaeria dothidea*.

AEC P-53

EXAMINATION OF THE QUALITY OF THE ENVIROMENTAL MEDIA IN REK OSLOMEJ

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The basic step towards improving the quality of the environment is quality and accurate data from the surveys of the relevant media and areas of the environment. Proper monitoring of water, air, soil and waste media changes from the large production facilities is necessary in order to identify and determine the possible pollution of the environment, thus providing the basis for adequate planning and improvement of the environment.

REK Oslomej – Kicevo is one of the largest thermal power facilities in R. Macedonia that has an impact on the environment.

In order to determine more detailed aspect at the environmental situation in the close surroundings of REK Oslomej, in the period 2017 and 2018, monitoring of the water, soil, waste and air media was made. The methodology used in conducting the tests is in accordance with the specific requirements stated in the applied standards and reference methods that are part of the scope of the accredited laboratory for environmental testing and safety at Technolab Skopje

This paper presents the results obtained from the analyzed parameters during the monitoring of the water, soil, waste and air media at the measuring points in the surrounding area of the REK Oslomej during the time periods determined according to the monitoring program.

Keywords: environment, water, soil, waste, air.

AEC P-54

DIFFERENTIATION OF MACEDONIAN TOBACCO USING MULTIELEMENT COMPOSITION - COMPARISON WITH CORRESPONDING SOIL

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Elemental composition of the oriental tobacco samples and corresponding soil extracts from three tobacco growing regions (Pelagonia, South east and Vardar Valley) were analyzed using multivariate statistical technique such as factor and cluster analyses. The main aim was to determine the correlation between the content of elements in tobacco samples and to investigate the possibility of differentiating production areas on the basis of element associations of tobacco leafs. Bivariate correlation was also used to establish the relationships between soil physical (pH, clay, cation exchange capacity - CEC, organic matters - OM) and chemical properties and element content in plant samples. Total and DTPA (diethylenetriaminepentaacetic acid) extractable content of following elements: Ag, Al, Ba, Cd, Cr, Cu, Li, Fe, Mn, Na, Ni, Pb, V, Sr, N, P, K and Zn were determined by atomic emission spectrometry with inductively coupled plasma (ICP-AES). Both soil and plant samples are well clustered according to their locality. According to the spatial distribution of the elements in tobacco leaves and corresponding soil, as well as the results of factor analyses, two geogenic, two mixed (geogenic-anthropogenic) and two anthropogenic associations were defined. Samples form Pelagonia region had highest content of Ba, Mg, Na and Sr that are strictly connected to the nature of the pedogenic materials and to the evolution processes of the different types of soil in this area. Content of Al, Cr, Cu, Fe and Mn are highest in the South East region where copper mine and flotation plant are located. Vardar Valley samples had highest content of Ca, Cd, Li, Ni, Pb and Zn, and this region is known for its lead and zinc industrial activity in the recent past. Compared to every studied element, only Mg has a statistically significant dependence between its content in soil and plant material. Negative correlation was observed between the elements that indicate anthropogenic contamination, K and Pb, Mn and V. Organic matters has significant positive correlation with content of Mn, Ba, Li and P in tobacco samples, pH with Ni, Cr and V content, and CEC had high correlation with Fe, Al and V.

Keywords: tobacco, soil, multivariate analysis, differentiation.

AEC P-55

PROTONATION OF CITRACONIC AND GLUTACONIC ACID IN AQUEOUS PERCHLORIC ACID SOLUTIONS

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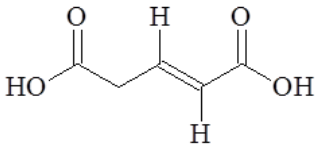
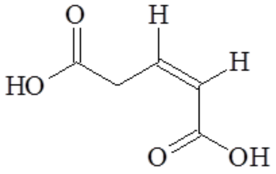
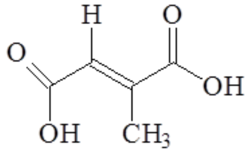
Citraconic and glutaconic acid acids are important industrial substances because of their wide practical application.



(*cis*-glutaconic)



(*trans*-glutaconic)



(citraconic acid)

The protonation process of these acids in concentrated perchloric acid media was followed by means of UV spectroscopy. The changes in the UV spectra of investigated organic acids were noticed with increasing the concentration of perchloric acid due to protonation reaction of glutaconic and citraconic acid. Namely, in strong acidic media the investigated acids act as weak organic bases and exist in their monoprotonated forms. In the case of citraconic acid at higher perchloric acid concentration the protonated anhydride was formed, as well. According to structure of investigated acids there are a few possibilities where the protonation can be attached. Thus, the partial atomic charges values calculated according to AM1 and PM3 semiempirical method was used to point out the possible sites where the protonation may take place. The thermodynamic dissociation constants were calculated using the methods of Yates and McClelland, Bunnett and Olsen, and „excess acidity“ function method. At the same time, the solvatation parameters *m*, m^* and *f* were evaluated. In order to correct the medium effect of the experimental spectra the method of characteristic vector analysis (CVA) was applied.

Keywords: citraconic acid, glutaconic acid, perchloric acid, ultraviolet spectroscopy, protonation, thermodynamic dissociation constants.

AEC P-56

VOLTAMMETRIC STUDY OF REDOX PROPERTIES OF BLOOD SERUM ISOLATED FROM MICE TREATED WITH ELECTROLYZED REDUCED WATER

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Electrolyzed reduced water (ERW) became significantly popular in the health care due to its antioxidative properties, its ability to fight against reactive oxygen species, thus to prevent many stress–related diseases. In this study, ERW was used in combination with other reducing agents, such as ascorbic acid and glutathione to treat three main groups of mice: (1) mice fed with ordinary water; (2) mice fed with ERW; and (3) mice fed with ERW enriched with ascorbic acid and glutathione (10^{-5} mol/L). The blood serum isolated over the period of three weeks from the three groups of mice was examined and compared using square–wave voltammetry (SWV) conducted at edge plane pyrolytic graphite electrode in a neutral phosphate buffer solution. Each of the three groups contained serums from 15 different mice, over the 3 weeks period, while each measurement was repeated three times to make the data statistically relevant. The voltammetric method was optimized by studying the effect deposition time, frequency, amplitude and step potential of the potential modulation.

After performing the analysis, the results were shown to differ in some key – response features obtained in the serum from the third mice group. In addition, statistical analysis has been performed to check if the three groups behave statistically different from each other.

Keywords: electrolyzed reduced water, square wave voltammetry, blood serum, glutathione, ascorbic acid.

AEC P-57

OPTIMIZATION OF SOLID-PHASE EXTRACTION FOLLOWED BY HPLC-DAD-MS CHARACTERIZATION OF HONEY POLYPHENOLS

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Polyphenols are secondary plant metabolites with well demonstrated beneficial effects for human health. Phenolic acids and flavonoids are the most important two classes of polyphenolic compounds that are present in plants and plant derived products. Honey is a highly concentrated aqueous solution of sugars (fructose and gluocose) and other minor constituents (organic acids, amino acids, proteins, polyphenolic compounds, vitamins etc.) that is well known fot its high nutritional and prophylactic value. Polyphenols are considered as valuable honey constituents as well as compounds that can be used as chemical markers for its botanical and geographical authentication and their analysis is a major analytical challenge. Analysis of polyphenols in honey includes their extraction from the complex sugar matrix, their separation and detection using liquid chromatography coupled with diode array detector (DAD) and mass spectrometry (MS).

In this study a solid-phase extraction procedure with Amberlite XAD-2 resin as a sorbent is optimized and tested on phenolic acids and flavonoids. The hydrophobic resin retains the polyphenols from the aqueous acidic honey solution, when passing through the column. Sugars are washed with water and then polyphenols are eluted with methanol. The obtained extract is concentrated by evaporation under reduced pressure and analyzed using reversed-phase HPLC-DAD-MS. The eficiency of the sample preparation procedure has been tested using standard solutions of phenolic acids and flavonoids in three concentation levels with recoveries for flavonoids reaching 88 % for rutin and 62% for naringenin and for phenolic acids around 90 % for hydroxycinnamic acids.

The method has been used for characterization of the polyphenolic profiles of Macedonian honey samples. The folowing polyphenols were found: phenolic acids (galic, chlorogenic, caffeic, *p*-coumaric, ferulic); flavanones and flavanonols (naringenin, pinocembrin); flavones and flavonols (chrysin, galangin, quercetin, apigenin) and the glycoside rutin. The developed methodology needs further validation for demonstration of its analytical parameters.

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Keywords: polyphenols, honey, solid-phase extraction, HPLC-DAD-MS.

AEC P-58

DEVELOPMENT OF REVERSED PHASE HPLC-DAD-MS METHOD FOR CHARACTERIZATION OF CANNABINOIDS IN HEMP OIL SAMPLES

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In recent years the scientific knowledge on the composition and the health benefits of hemp and its edible products has considerably increased. Hemp seed oil has been promoted as a good source of nutritious omega-6 and omega-3 polyunsaturated acids as well as variable quantities and ratios of different cannabinoids that are the main biologically active cannabis components. They comprise a complex group of closely related compounds, of which 70 are well described, but only around 10 are mostly abundant and usually characterized.

Medical marijuana generally possesses high levels of the therapeutic cannabidiol, CBD, and lower levels (generally less than 0.3%) of the psychotropic tetrahydrocannabinol, d9-THC. The primary focus of the analytical methodology has been primarily put on THC for its pharmacological and toxicological relevance and strict legal limits have been enforced. But, other cannabinoids, primarily CBD provide unique biological activities such as anticonvulsive, anti-epileptic, and antimicrobial properties.

For these reasons, efficient analytical methods are necessary for characterization of cannabinioids in the variety of hemp oil products that have appeared on the market as well as for their quality control during production. In this work, a fast and simple method has been developed and applied for separation of cannabinoids in hemp oils from the market using C18 column (250x4.6 mm, 5 μm particle diameter) and gradient elution with water and acetonitrile. UV diode array detection together with mass spectrometry has been used for structure elucidation of the separated cannabinoids with focus on characterization of CBD and THC.

Keywords: cannabinoids, cannabidiol, d9-tetrahydrocannabinol, HPLC-DAD-MS.

Physical, Structural Chemistry, Spectroscopy and Electrochemistry (PSSE)

PSSE O-1

SOL-GELS IN PROTEOMICS APPLICATIONS

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Sol-gels offer wide-range working area for different applications. Also synthesis of sol-gel materials could be possible in mild conditions that is supplied many advantages for the applications especially biomolecules which are active mainly in physiological pHs. Many different synthesis routes and starting materials namely precursors for the sol-gels are possible and in this way it is possible to synthesize any sol-gel materials for a large variety application. For many different biological applications such as analysis of non-covalent complexes, macromolecules, post-translational modifications and mainly proteomics studies, soft ionization mass spectrometric techniques which are Matrix-assisted Laser Desorption/Ionization-Mass Spectrometry (MALDI-MS), Electrospray Ionization-Mass Spectrometry (ESI-MS) and also newly Ion Mobility-Mass Spectrometry (IM-MS) have been used very widely in recent years. Although the advantages of these mass spectrometric techniques, different sample preparations have to be applied for the complex samples to perform analyses of the post-translational modifications of proteins prior to the mass spectrometric analysis. In this communication, it will have discussed the synthesis of different types of sol-gels showing specific affinity to the different functional group modified biomolecules and the applications of these sol-gels for the targeted biomolecules to perform specific separation and high enrichment capacity prior to mass spectrometric analysis. Different transition metal ion based sol-gels were synthesized, characterized using Fourier Transform-Infrared (FT-IR) Spectrometry, X-Ray Diffraction Spectrometry and Scanning Electron Microscope (SEM) and then used especially for analysis of the different post-translational modification of proteins. Experimental conditions during the sol-gel synthesis were adjusted in order to arrange some properties of sol-gels such as roughness, hydrophilicity, pore-size, surface pKa and the size of the particulates. Specificity and selectivity of the synthesized sol-gels was tested for different post-translational modified proteins in the analyses of different World-wide samples.

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Keywords: sol-gel, mass spectrometry, post-translational modifications, specific enrichment.

PSSE O-2

FABRICATION AND APPLICATIONS OF NANOPOROUS MATERIALS

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Nanoporous structures formed in solid materials can be used in various separation techniques and sensing applications for different types of molecules[1]. Depending on the desired application, these structures can be prepared on synthetic materials as multipores and even single nanopores. Single nanopores are usually used for the detection, determination and separation of analytes, while multipores are mostly used in mass transport studies for possible applications such as sensors or bio-separators[2].

Various techniques and materials can be used to improve the sensing paradigm. Among the fabrication techniques, track-etching of polymer membranes is an easy, cost-effective and reproducible method that enable controlled pore size and geometry[3]. Similarly, fabrication of glass nanopipettes is also possible for obtaining nanopores with desired sizes. The track-etch method is essentially based on the irradiation of materials such as films and membranes with heavy ions. During the irradiation process, ions leave latent tracks along their trajectories and these tracks are then electrochemically etched to fabricate nanopore(s). The fabrication of glass nanopipettes on the other hand, is based on the pulling of glass capillaries at high temperatures by a laser puller. After the pulling process, two identical pipette tips, in nano or micro scale, can be obtained and used without any additional step[4].

In this work we describe the preparation of single and multiple nanopores on polymer membranes using track-etching method and also quartz nanopipettes. Some example applications of both the nanoporous polymers and nanopipettes are given such as DNA detection, mass transport of charged molecules and metal ion detection. Our studies include electrochemically determining pore geometry, measuring electric field near the nanopore tip using simulations and experimentally determining the rate of mass transport and pore selectivity under various conditions of particle charge, temperature, pore geometry and applied potential.

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Keywords: Nanopores, track-etching, nanopipettes, resistive-pulse sensing, mass transport.

PSSE O-3

IODIDE···π INTERACTIONS OF PERHALOGENATED QUINONES IN CO-CRYSTALS WITH ORGANIC BASES

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A series of cocrystals of tetrachloro- and tetrabromoquinone with organic iodide salts has been prepared and structurally characterised. Derivatives *N*-methylpyridinium were chosen as cations, due to their planarity and similar size to the quinones, while their electronic properties are radically different. While the iodide usually acts as an electron donor, reducing the quinone into the semiquinone radical, in the present study we obtained co-crystals of the neutral quinone and the iodide anion.

In the studied crystals, the common motive is a sandwich-like I^-···quinone···I^- moiety with close contacts between the iodide anion and carbon skeleton of the quinoid ring. Distances between the iodide and the ring centroid range between 3.60 and 3.85 Å, which is slightly shorter than sum of van der Waals radii for C and I. Interactions between π system aromatic ring and an anion are rarely observed, since aromatics are usually electron-rich; in the case of electron-depleted quinoid rings, anion···π contacts are more likely to form. In the studied cases, however, there is also a partial electron transfer between the iodide and the quinone which is noted by a change of colour: the neutral quinone is yellow, while the co-crystals and the semiquinone crystals are black.

The charge transfer was studied in detail by a combination of IR and solid-state NMR spectroscopies and quantum chemical methods.

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Keywords: charge transfer; anion...pi interactions; crystal engineering; quinones.

PSSE O-4

HALOGEN BOND AS A RIVAL TO HYDROGEN BOND IN CRYSTAL ENGINEERING – COCRYSTALS OF N-HALOGENOIMIDES

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Over the past couple of decades, the importance of halogen bonds (XB) in crystal engineering is constantly increasing. This is predominantly due to their strength and directionality which are commonly claimed to be close to those of hydrogen bonds – the generally accepted benchmark for evaluation of intermolecular interactions in supramolecular chemistry and crystal engineering.

Recently, *N*-halogenated imides, common halogenating agents in organic synthesis, have been marked as extremely strong halogen donors. In our studies, we have conducted an extensive study on the effect of the halogen type as well as the basicity (nucleophilicity) of the halogen acceptor in *N*-halogenated succinimide cocrystals with pyridine derivatives of different basicities. These studies have shown *N*-halogenated succinimides to form short XBs with the presented donors with the bond energies decreasing with the decrease of the pyridine basicity and with decreasing size of the halogen (I>Br>Cl). The use of imides allowed for a direct comparison between halogen bonding (with *N*-halosuccinimides) and hydrogen bonding with unmodified succinimide, which has revealed that the hydrogen bond is in fact weaker than the halogen bond with iodine, and comparable to that with bromine. [1]

Employing different imides can change the potential of forming other interactions – when *N*-halogenated phthalimides are used as XB donors, weak hydrogen bonds form which might complement, or compete with, the primary halogen bond formed by the imide and a XB acceptor.[2] Particularly interesting are cocrystals formed by *N*-halogenimides and pyridines possessing additional halogen (or hydrogen) bond donor groups. The halogen atom of the *N*-haloimide binds preferentially to the pyridine nitrogen, while the halogen of the pyridine ring forms only substantially longer halogen bond with the *N*-haloimide oxygen atoms, other halogen atoms, or π-systems. This hierarchy is maintained even if the *N*-haloimide halogen is a lighter one than the one on the pyridine ring following the molecular electrostatic potential; the highest positive values of ESP being associated with the best XB-donor atoms. In cocrystals of *N*-iodoimides with aminopyridines, the imide and pyridine nitrogen also bind through a very short N–I···N halogen bond, while the amino group participates in N–H···O – hydrogen bonds with imine oxygen atoms, in much the same way as aromatic groups form C–H···O interactions in equivalent structures without strong hydrogen donors. The dominant interaction in all structures is clearly the halogen bond with the *N*-haloimide as the donor. In this way we were able to study the subtle interplay of halogen and hydrogen bond.

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Keywords: halogen bond, imide, crystal engineering, cocrystal.

PSSE O-5

DEACTIVATION ASPECTS OF METHANOLYSIS CATALYST BASED ON CAO LOADED ON MESOPOROUS CARRIER

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Not presented.

PSSE O-6

NANO-STRUCTURED MATERIALS AND THEIR APPLICATION IN THE DETECTION OF BIOLOGICAL COMPOUNDS

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Nanoscale materials nowadays represent a widely investigated research area. With the development of controlled synthesis and uniform materials characteristics, their high potential is being realized to the maximum. The results presented in this short review clearly point out that an expansive amount of structural, chemical and electrochemical data about materials is available in field of electroanalytical chemistry and chemical sensors and biosensors. It is shown that adequate material synthesis with unique characteristics can improve detection of biological active compounds in terms of simplicity, sensitivity and selectivity.

State-of-the-art research in this field is focused on the application of novel synthesized nanomaterials as electrode materials. Common solid-state electrodes show satisfactory characteristics for the quantification of biologically active components, but also have some drawbacks, including adsorption of tested compounds on electrode surface. This signifies surface cleaning and electrode renewal would be necessary, but since these practices are difficult or impossible to implement, electrode use is limited to one measurement. These facts have encouraged the application of different novel nanomaterials for solid electrodes and investigation of their performance in real sample analysis.

The combing of different materials at nanoscale, opens numerous possibilities to fabricate different surface with unique properties. These materials, in recent years, have shown high potential in the field of electrochemistry and electroanalytical chemistry of biologically active compounds. The aim of this work is to show recent progress and application of nanostructured materials as electrochemical sensors and biosensors.

Keywords: nano materials, electrochemical sensors and biosensors.

PSSE O-7

ARYLDIAZONIUM INTERACTION/CHEMICAL GRAFTING ON GRAPHYNE AND GRAPHYDINE STRUCTURES VIA ‘’AB INITIO’’ CALCULATIONS

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The large family of nanocarbon allotrope materials: 0D (fullerenes, quantum dots, graphene dots, carbon dots, onion-like carbon, nanodiamonds), 1D (single-walled and multi-walled nanotubes, nanohorns), 2D (graphene, multilayered graphitic sheets, graphene oxide) and 3D (graphite), recently endorsed its newest members – graphyne (GRPH) and graphdyine (GRPD). The one-atom-thick 2D materials are composed entirely of sp and sp^2 carbon atoms, in which the nearby benzene rings are linked in a network by one (in graphyne) or two acetylenic (-C≡C-) groups (graphdyine) (Figure 1). The structure gives these materials interesting properties such as extreme hardness, very high electric conductivity, high thermal resistance, etc. Foreseen applications include gas separation, lithium storage, as a possible replacement material for silicon transistor technology, etc.

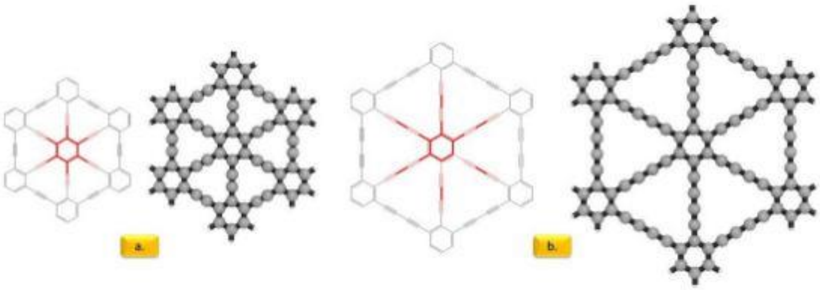

Figure 1. a.graphyne (GRPH) and b. graphdyine (GRPD) structures used in ‘’ab initio’’ calculations.

To span, their use in many other potential applications (i.e to increase their solubility, to add anchoring groups that enable these structures to be linked with nanoparticles or with the different substrates, etc), the GRPH, GRPD surface needs to undergo chemical modifications. As the diazonium grafting strategy [1] is the most straightforward and easiest one to be applied for surface grafting reactions, we explored this strategy using ‘’ab initio’’ calculations. To decrease the computational costs, prior to the use of the DFT calculations, molecular mechanics (MM) and dynamics (MD) were performed. For initial geometry optimization in MM, the COMPASS II forcefield was employed. The optimized structure from MD simulations (NVT ensemble coupled with Nose thermostat) served as the initial structure for the DFT/6-311+g(d,p)/Grimme D3 evaluation of the interaction energy of GRPH, GRPD (onto three chosen adsorption sites) and the three p-substituted aryldiazonium sats (R=-H, $-CH_3$ and $–NO_2$) with +I and –I inductive effects. Non Covalent interactions were analyzed by Reduced Gradient Density (RDG) using Multiwfn and VMD software. The Bond Dissociation Energies (BDE) were calculated from the energy difference between the grafted GRPH or GRPD structures with phenyl moieties and the energy sum of the GRPH or GRPD and the corresponding phenyl radicals.

Keywords: quantum mechanics, molecular dynamics, graphdyine, non-covalent interactions, DFT.

PSSE O-8

RECENT MODEL DEVELOPMENT IN THEORETICAL ELECTROCHEMISTRY IN ORDER TO CLOSE THE APPARENT COMMUNITY GAP BETWEEN ELECTROCATALYSIS AND BATTERY RESEARCH

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Atomic scale-insights into the performance of electrode materials or solid-state catalysts require thermodynamic considerations as first step in order to determine potential surface structures that are relevant for subsequent kinetic studies.[1] In heterogeneous catalysis as well as electrocatalysis, the *ab initio* atomistic thermodynamics approach[2] has been recognized as powerful tool by compiling thermodynamically stable surface phases as function of the corresponding environmental parameters in the form of stability diagrams or by *a priori* computational screening in order to propose promising (electro-)catalysts by the construction of Volcano plots.[3]

Quite in contrast, the *ab initio* thermodynamics approach has been introduced in battery research only recently by transferring the concept of surface Pourbaix diagrams from electrocatalysis to lithium-ion batteries.[4] In this talk, recent investigations that aim at applying well-established concepts such as stability diagramsor Volcano plots from the field of (electro-)catalysis for the investigation of electrode materials in lithium-ion batteries are presented and critically discussed.[5,6]

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Keywords: ab initio thermodynamics, lithium-ion batteries, catalysis.

PSSE O-9

TEMPERATURE DEPENDENCE OF RADIATIVE LIFETIMES, OPTICAL AND ELECTRONIC PROPERTIES OF SILICON NANOCRYSTALS CAPPED WITH VARIOUS ORGANIC LIGANDS

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Despite the known temperature effects on the optical and photoluminescence properties of silicon nanocrystals (Si NCs), most of the density functional theory (DFT) calculations thus far have been carried out at zero temperature, i.e. fixed atomicpositions. We present a study of the effect of finite temperature on the radiativelifetimes and band gaps of Si NCs capped with six different organic ligands, CH_3, C_2H_5, C_2H_4Cl, C_2H_4OH, C_2H_4SH, and $C_2H_4NH_2$. In addition, we show the differences in electronic and optical properties, as well as the wavefunctions (WF) around the band gap, of the capped Si NCs at zero temperature. We show that the NCs capped with alkyl and C_2H_4Cl ligands have larger HOMO-LUMO and opticalabsorption gaps compared to the $C_2H_4NH_2$, C_2H_4OH, and C_2H_4SH capped NCs.We demonstrate that this big difference in both gaps comes from the increasedcontribution to the states at the top of the valence band from the NH_2, OH and SH groups of the $C_2H_4NH_2$, C_2H_4OH, and C_2H_4SH ligands, respectively. Additionally, we assigned the rather weak dependence of the radiative lifetimes of $C_2H_4NH_2$ capped NCs on the NC size to the slightly changing symmetry of the highly localized HOMO WF at the NH_2 group. Furthermore, we demonstrate that the temperatureeffect on the radiative lifetimes and band gaps is larger in alkyl and C_2H_4Cl capped Si NCs. We indicate that the decrease in radiative lifetime of the CH_3 capped NCswith increasing temperature comes from the changing symmetry of the LUMO WFand the increased dipolar overlap between the HOMO and LUMO WFs. Lastly, weshow that there is a constant decrease in the band gaps of the Si NCs with increasing size, with the band gap change of CH_3 capped NCs being larger compared tothe band gap change of the $C_2H_4NH_2$ capped NCs.

Keywords: Si nanocrystals, passivation, organic ligands, band gap, radiative lifetime, DFT.

PSSE O-10

EFFICIENCY OF INDIRECT ELECTROLYTIC DEGRADATION OF SULFAMETHAZINE BY FENTON'S REAGENT GENERATED AT CARBON SPONGE, CARBON FELT, AND STAINLESS STEEL CATHODE

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The development of waste water treatment technology has led to different pollutants removal methods, such as biological, physical, and chemical ones. Among these, electro-Fenton is a relatively newly developed method with high capacity for organic pollutants destruction [1]. It makes use of Fenton's reagent generated electrochemically on a cathode in an electrolytic cell where the polluted water is put. Fenton's reagent is a mixture of hydrogen peroxide H_2O_2 and iron II ions Fe^{2+} which react at pH 3 to give hydroxyl radicals $^{\bullet}OH$, a very powerful oxidizing agent. Then $^{\bullet}OH$ being a strong oxidant, oxidizes organic pollutants present in the solution. H_2O_2 is created continuously during electrolysis from the reduction of oxygen on cathode, whereas Fe^{2+} is added in small catalytic quantities as a sulphate salt. Fe^{2+} is oxidized to Fe^{3+} in the reaction with H_2O_2, but instantly it reduces to Fe^{2+} on cathode, thus the concentration of Fe^{2+} is not altered significantly during the process [1,2].

It has been observed that SMT represents adverse effects to some organisms [3-5]. In this study the degradation of sulfamethazine (SMT) (oxidation to byproducts) and mineralization (oxidation until CO_2 and H_2O) with carbon sponge, carbon felt, and stainless steel cathode has been investigated, as well as the energy consumption evolution during time and charge passage. The performance of each cathode was evaluated towards SMT degradation. The concentration of SMT during electrolysis was followed by HPLC. It was found that the degradation of SMT was complete and quick with carbon sponge cathode. Carbon felt cathode showed slower degradation reaction towards SMT but it still was efficient. The degradation rate when stainless steel was used decreased considerably because of its small surface area, which did not provide high amounts of H_2O_2. In fact hydrogen peroxide production experiments revealed that stainless steel could produce almost inconsiderable quantity of H_2O_2. In this case one can say that most of the SMT degradation was due to its oxidation on anode. The mineralization extent of SMT was measured by a TOC measuring device. Here again the carbon sponge cathode was the most efficient and stainless steel the less performing one. Over 90% of SMT TOC removal was achieved with carbon sponge cathode.

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Acknowledgements: France embassy in Kosovo.

Keywords: pollutant, sulfamethazine, electro-Fenton, cathode, carbon sponge, degradation.

PSSE O-11

A THEORETICAL AND EXPERIMENTAL SQUARE-WAVE VOLTAMMETRIC STUDY OF ASCORBIC ACID IN THE LIGHT OF MULTI-STEP ELECTRON TRANSFER MECHANISM

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A detailed theoretical model of the complex two-step redox mechanism of ascorbic acid coupled with chemically irreversible fast follow-up chemical reaction (hydrolysis of dehydroascorbic acid) in aqueous solution by square-wave voltammetry is presented. A well known apparently electrochemically irreversible oxidation of ascorbic acid in aqueous solutions is associated with a single irreversible anodic peak, representing two consecutive one-electron transfer processes, coupled with a fast follow up irreversible chemical reaction to the final electro-inactive product. However, under experimental conditions of the fast square-wave voltammetry (SWV) the electrode process appears quasireversible, with a small backward (reductive) voltammetric component, representing the reduction of at least one of the reaction intermediates. To provide an insight into the complex electrode mechanism, a theoretical model was made assuming two electron transfer steps (the first is quasireversible, the second is electrochemically reversible), coupled with follow-up chemically irreversible chemical reaction. The model enables estimation of the role of variety parameters affecting the morphological evolution of the voltammograms, such as formal potentials difference of the two steps, and the kinetics of the follow-up chemical reaction. Moreover, it has been shown that the properties of the response markedly depend on the amplitude and frequency of the potential modulation, which has been studied in detail both theoretically and experimentally. Theoretical square-wave voltammograms were qualitatively compared with experimental SW voltammograms of aqueous solution of ascorbic acid at edge-plane pyrolytic graphite electrode (EPPGE) in a phosphate buffer solution at pH = 7.

Keywords: square-wave voltammetry, theoretical model, ascorbic acid, two-electron transfer steps, quasireversible, EPPGE.

PSSE O-12

THE ELECTROCHEMISTRY AS A GENERAL TOOL TO UNRAVEL THE ELECTRONIC STRUCTURE AND THE (PHOTO)ELECTROCATALYTIC PROPERTIES OF NANOSTRUCTURED TITANIUM DIOXIDE

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Titanium dioxide is a low-cost material characterized with multifunctional properties and many important applications. Among the most investigated are its application in environmental remediation (air and water purification), energy production, accumulation and saving. Also it can be applied in self-cleaning coatings, antifogging surfaces and gas sensing devices. Fundamental understanding and innovative design of TiO_2 materials are very important in order to improve the performances of all the devices based on this material.

In this work the electronic, and the (photo)electrochemical properties of nanostructured TiO_2 with different crystalline phase (anatase and rutile) and morphology (nanowires, nanoparticles, nanotubes, nanocolumns and nanofibers) were investigated. TiO_2 thin film electrodes were prepared on conducting glass (glass sheet covered with a thin film of F-doped SnO_2) employing various preparation methods (chemical bath deposition, hydrothermal synthesis and anodization of titanium foil).

The electronic structure of nanostructured TiO_2 nanowires (band gap energy, conduction band edge, and distribution of surface trap states) was successfully determined by employing photoelectrochemical methods (chronoamperometry and cyclic voltammetry). These measurements evidence the existence of an exponential surface state distribution just below the conduction band in the case of anatase. The situation is rather different for rutile, where these states are absent. In both cases, additional band gap monoenergetic states associated to grain boundaries are present. Their energetic location depends on the crystalline phase. The density and energetic location of grain boundary trap states are highly dependent, not only on the crystalline structure (whether anatase or rutile), but also on the electrode morphology (determining the facets that meet at the grain boundaries).

The photoelectrochemical and photocatalytic properties of nanostructured TiO_2 electrodes having different crystalline phase (anatase and rutile), have been investigated in acidic medium (0.1 M $HClO_4$) by means of electrochemical techniques. The photooxidation of water, methanol and formic acid have been studied. According to the photoelectrochemical measurements the reduction of particle size seems more beneficial for the prutile than for anatase. On the other hand, the open circuit measurements point out that anatase NWs are better photocatalyst for both methanol and formic acid oxidation in acidic medium.

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Keywords: titanium dioxide, thin films, chemical bath deposition, hydrothermal synthesis, photoelectrochemical properties, photocatalysis, bandgap, electronic states.

PSSE O-13

HOW HEAVY IS HEAVY MAGNESIUM CARBONATE – TETRAHYDRATE OR PENTAHYDRATE?

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Magnesium carbonate in nature exists in several different forms: anhydrous, hydrates and basic forms, all of which are used for different applications. In the pharmaceutical industry, basic forms denoted as magnesium carbonate heavy are mainly used for formulation of preparations for neutralizing excess of stomach acid and relieving heartburn. They are denoted as heavy due to the higher bulk density than the light magnesium carbonates, but this epithet is often mistaken to be describing the content of water molecules in the structure of basic magnesium carbonates.

For most of its applications, the precise molecular structure and molecular weight of magnesium carbonate heavy is not necessary. Nevertheless, in pharmaceutical industry, especially in formulations where it is used as API (Active Pharmaceutical Ingredient), knowing the crystal structure and precise molecular weight of magnesium carbonate heavy is essential since it is used in order to calculate its assay in the finished dosage form. Therefore, extensive structural characterization was carried out using thermal analysis methods such as Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG/DTG), temperature-resolved Fourier-Transform Infrared (FTIR) spectroscopy and X-Ray Powder Diffraction (XRPD). Different batches from different manufacturers of magnesium carbonate heavy were analyzed and by obtaining relevant data for the water content, the molecular weight of magnesium carbonate heavy was determined.

Keywords: magnesium carbonate, XRPD, FTIR, thermal analysis.

PSSE P-1

ELECTROCHEMICAL DETECTION OF ASCORBIC ACID IN THE PRESENCE OF SODIUM DODECYLBENZENESULFONATE

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Ascorbic acid (AA) is an essential water-soluble vitamin for the human nutrition, as an antioxidant found in many biological systems and foods. Many analytical methods have been reported for the determination of vitamin C. A method for the detection of ascorbic acid (AA) was developed using cyclic voltammetry (CV) analysis with three metallic electrodes (Pt-work, Pt-counter and Ag wire – indicative). From the results, the determination of ascorbic acid (by measuring the oxidation currents) can be performed in wide range of concentrations from 1-600 mM with excellent regression coefficient up to 0.995, moreover our results indicate that the system can be applied directly to measure the content of this molecule in real samples without any prior treatment of the samples. The results prove that this technique has been more and more preferred to the previously applied methods, as it is characterized by accuracy, rapidity and also by the simplicity of the use of the required procedure.

Keywords: cyclic voltammetry, vitamin C, limit of detection, electrochemical detection.

PSSE P-2

EXPERIMENTAL AND MONTE CARLO SIMULATION STUDY OF ALDRIN ADSORPTION ON RUTILE SURFACE

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The adsorption of Aldrin (organochlorine pesticide) is calculated experimentally and by Monte Carlo (MC) simulations. The GC-ECD method is used to determine the adsorption capacity of TiO_2 microparticles. The experimental study included both: a. bare and b. surface modified rutile. In the second case prior its use for adsorption study, rutile underwent surface modification reaction by ultrasonic dediazonation reaction of the aryldiazonium salts. These salts were synthesized by diazotization of corresponding arylamines. Monte Carlo simulations using Dreiding force field were performed onto 8x8 slab model of rutile [on three crystallographic planes: {100}, {101}, and {001}] surface (with a 40 Å vacuum on the C axis) in the presence and the absence of 300 solvent (hexane).

Keywords: rutile, Monte Carlo, pesticide, Dreiding force field.

PSSE P-3

MONTE CARLO SIMULATION STUDIES TOWARD THE UNDERSTANDING OF THE SOLVENT/SOLUTE INTERACTION BETWEEN THE OXYGEN MOLECULES FORMED BY SECM ONTO Fe(001) SURFACE

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The Fe(001)/O_2(molecules)/solvent/solute represents an interesting interface that can provide fundamental insight toward for the elucidation of many natural processes occurring at the surface of this material. Such interface types in many aspects play a crucial role in the planet's biogeochemical cycles, ecosystem functioning, agriculture, as well as industry. A key to understanding this interface apart from the use of instrumental techniques is the use of Monte Carlo simulations.

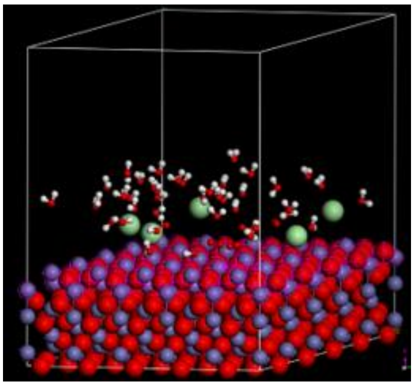

Figure 1. Slab model of Fe(001) surface together with chloride ions, oxygen molecules and water molecules.

Monte Carlo (MC) simulation [using COMPASS II force field performed onto Fe(001) slab models (Figure 1) with a 60 Å space along C axis occupied by: 1 to 10 Cl^- or Na^+ ; 40 to 50 water molecules and 1 to 10 oxygen molecules] studies were applied to search for the lowest energy configurational space of Fe(001) / solute/solvent interface . The most stable pose from MC calculations, is used for the Molecular Dynamics (MD) simulations, in NVT ensemble coupled with NHL thermostat, with a total simulation time of 300 ps and 1fs time step at T=298 K. The analysis of the frames from MD gave important details regarding the organization of O_2 molecules at the interface and the impact of analyzed ions and water molecules on this structuring.

Keywords: Fe(001), molecular dynamics, SECM, Monte Carlo, oxygen.

PSSE P-4

EFFECT OF TIME, BUBBLE DIAMETER AND pH VALUE ON THE ELECTROCHEMICAL BEHAVIOR OF OXYGEN BUBBLE EMERGED ON HEMATITE AND GOLD ELECTRODE

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The electrochemical properties of gas bubbles on hematite/water interfaces play important roles in a variety of natural and technological processes. It contributes to several biogeochemical cycles playing an important role as an electrocatalyst in renewable energy researchers and its considered among others also for photo-assisted water splitting reactions, in the fabrication of gas sensing electrodes, foam fractionation, food processing, and purification processes.

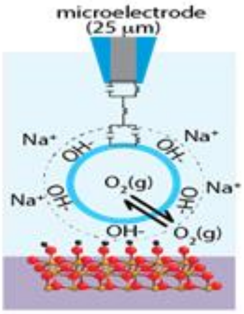

Figure 1. The schematic representation of the system containing the O_2 bubble sandwiched between the 25 µm SECM tip / Fe(001) surface together with the equivalent circuit model used for EIS measurements. Picture adapted from Boily's group for oxygen bubble/water interface.

Prior to the measurements, the pH value of the solution (containing sodium chloride) was adjusted to 4 and 7. For the measurements the ultramicroelectrode tip was approached to the surface of the oxygen bubble, squeezing the bubble and after that EIS measurements were performed. The bubbles formed on hematite (by SECM tip) were typically 100 ~ 900 µm wide. For the characterization of the interactions between ultramicroelectrode and oxygen bubble/hematite cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used. The key relationships between time and electrochemical response on EIS measurements included the increase of resistance by the bubble and charge transfer resistance with time domain.

Keywords: oxygen bubble, hematite, gold, electrochemical impedance spectroscopy.

PSSE P-5

CARBOXYLATED GRAPHENE OXIDE AS A CORROSION INHIBITOR FOR TANTALUM METAL – AN EXPERIMENTAL AND “*ab initio*” STUDY

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The inhibition effect of Carboxylated Graphene Oxide (C-GOx) on the corrosion of tantalum in 0.1 mo/dm^3 sulfuric acid solution was investigated using Electrochemical Impedance Spectroscopy (EIS) measurements. The presence of C-GOx in the corrosion media suppressed the corrosion rate of tantalum metal. Different quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), Hirshfeld charges and dipole moment (μ), were calculated for C-GOx in order to gain insights regarding the adsorption of this material onto ta surface. Additionally, Monte Carlo (MC) simulation (using Universal force field/ 1 or 2 molecule of C-GOx / slab models with a 60 Å space along C axis occupied by: 300 water molecules, 50 H_3O^+ and 50 SO_4^{2-} ions) studies were applied to search for the best configurational space of C-GOx / tantalum system [two different crystallographic planes Ta(001), and Ta(100)]. The interaction is also analyzed in details by performing Molecular Dynamics (MD) simulations using Universal forcefield (charge assignment with QEq_charged1.1 technique), in NVT ensemble coupled with Berendsen thermostat, with a total simulation time of 300 ps and 1fs time step at T=298 K.

Keywords: molecular dynamics, Monte Carlo, tantalum, carboxylated graphene oxide.

PSSE P-6

EXPERIMENTAL AND COMPUTATIONAL EVALUATION OF *n*-ALKANOIC ACIDS AS A CORROSION INHIBITOR NIOBIUM IN SULFURIC ACID SOLUTION

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The inhibition effect of n-alkanoic acids with increasing chain length (hexanoic-, heptanoic-, nonanoic and decanoic acids) on the corrosion of niobium in 0.1 mo/dm^3 sulfuric acid solution was investigated using electrochemical measurements. The polarization curves indicated that n-alkanoic (depending on their chain length) behaved as a mixed-type inhibitor, affecting both cathodic and anodic corrosion currents. Quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), Hirshfeld charges and dipole moment (µ), were calculated. Additionally, Monte Carlo (MC) simulation (using Universal force field/ 1 molecule of n-alkanoic acids/ slab models with a 40 Å space along C axis occupied by: 200 water molecules, 30 H_3O^+ and 30 SO_4^{2-} ions) studies were applied to search for the best configurational space of n-alkanoic acids/niobium system [three different crystallographic planes Nb(001), Nb(010), Nb(100)].

Keywords: corrosion inhibition, Monte Carlo, *n*-alkanoic acids, niobium.

PSSE P-7

EXPERIMENTAL, THEORETICAL (DFT) AND MONTE CARLO SIMULATION OF ALDRIN ADSORPTION ONTO BARE AND MODIFIED GRAPHITE SURFACE

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Organochlorine pesticides have been widely used in the past, but Aldrin, DDT, dieldrin, and endrin have been banned from use as a pesticide. However, the continued persistence and wide distribution of these substances in the environment remains a concern. Both aldrin and dieldrin affect the central nervous system, producing irritability, tremors, and convulsions. The purpose of this research was to analyze and compare the ability of graphite flakes and modified graphite on the absorption of Aldrin. First, the synthesis of diazonium salts was performed, more precisely, the synthesis of two aryl diazonium salts bearing nitrophenyl and carboxyphenyl moieties. Graphite surface was modified through various groups, and the adsorption ability was investigated. GC/ECD was used to evaluate the ability of the bare and modified graphite flakes for the adsorption of the Aldrin molecule.

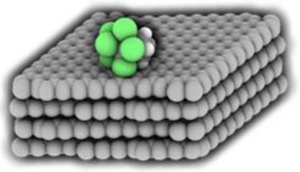

Figure 1. Graphite periodic slab model (with adsorbed Aldrin molecule) used for Monte Carlo simulations.

Monte Carlo simulations (Figure 1) and DFT calculations were successfully applied to gain insights at molecular level concerning the adsorption of this molecule. The calculations allowed us to determine positions in which the energy of adsorption is highest. The calculations offered important details, regarding the interaction geometry of Aldrin molecule after its adsorption onto bare/modified graphite surface.

PSSE P-8

MONTE CARLO SIMULATIONS AND EXPERIMENTAL STUDY OF THE ALDRIN ADSORPTION ONTO GRAPHENE SURFACE MODIFIED WITH SUBSTITUTED PHENYL LAYERS

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Pesticides are chemical compounds, widely used in many agricultural areas, in the prevention and control of harmful organisms. The introduction of pesticides in agriculture was of great importance because their utilization led to the reduction of the adverse effects of diseases in crops and plants, which allowed an increase in the production. On the other hand, commercial pesticide use has the potential to contribute to significant risk to the environment and human symptomatic illnesses. These may result from direct pesticide contact during application as well as from mobile or persistent pesticides that remain in the soil which can over time enter groundwater and drinking water supplies. Water treatment facilities employ a number of treatment techniques to reduce potentially harmful and disruptive contaminants, such as pesticides. An effective technique to get rid of these pollutants from water, includes, but is not limited to, adsorption of pesticides onto graphene and modified graphene (as proposed in this study).

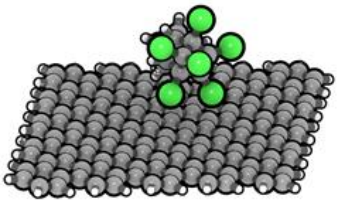

Figure 1. Optimized structure of the 5x5 finite-size Armchair graphene model with the adsorbed Aldrin molecule.

To gain information on the molecular level regarding: a) the nature of the interaction, b) interaction strength and c) one the impact of substituted phenyl groups on the nature and interaction energy between the graphene surface (three 5x5 finite-size single graphene sheets models: Zigzag, Armchair, Zigzag/Armchair) and Aldrin molecule, Monte Carlo simulations and DFTB calculations were employed in the study. Moreover, DFT/B3LYP calculations were also accomplished to estimate and visualize the NCI (noncovalent interactions) among the graphene models and the Aldrin molecule.

Keywords: grapheme, aldrin, adsorption, diazonium salts, GC-ECD; FT-IR; ATR; Monte Carlo simulations.

PSSE P-9

“*Ab Initio*” AND EXPERIMENTAL EVALUATION OF THE ALDRIN ADSORPTION ONTO BARE AND COVALENTLY MODIFIED GRAPHENE OXIDE SURFACE

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Pesticides have a long-time history of being used for the improvement of agricultural productivity. Because of that people through different ways are exposed to low levels of pesticides, some of which are toxic and often related to illness.

The aim of this study the use of materials with a large surface area for facilitating the removal of chlorinated pesticides (Aldrin) by adsorption. Two materials were tested for adsorption of Aldrin: bare synthesized graphene oxide and covalently modified graphene oxide (with substituted phenyl layers bearing functional groups with increased polarity).

Characterization of the synthesized graphene oxide, aryldiazonium salts (used for surface modification reactions), and covalently modified graphene oxide was performed by ATR-IR spectroscopy. GC-ECD chromatography was used for analysis of adsorptive properties of GOx and modified GOx-aryl-R surfaces.

Molecular mechanics (COMPASS II forcefield) and DFTB (Density Functional Tight-Binding) calculations were employed to evaluate the interaction energies between the graphene oxide and the Aldrin molecule. The calculated values for the adsorption energy pointed out to a strong nature of the interaction of the Aldrin molecule with graphene oxide surface.

PSSE P-10

DFT AND MD STUDY OF THE INTERACTION OF SOME SUBSTITUTED ARYL DIAZONIUM CATIONS WITH GRAPHENE OXIDE

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The research is oriented to evaluate the interaction energy between graphene oxide (GOx) and four different substituted aryl diazonium cations using DFT (Density Functional Theory) and MD (Molecular Dynamics). The GOx structure was approximated using a 4x4graphene model (Figure 1) that has: two epoxy-, six carboxy- and two hydroxy- functional groups.

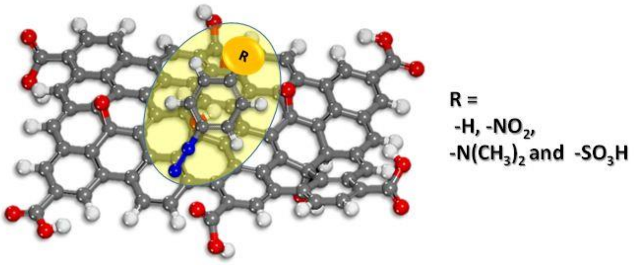

Figure 1. Representation of the used Graphene oxide 3D molecular model with substituted aryldiazonium cation.

Prior to DFT calculations, in order to decrease the computational cost for the calculation of the interaction energy, the GOx underwent MD calculations using COMPASS II forcefield (charge assignment with QEq_charged1.1 technique), NVT ensemble coupled with NHL thermostat, with 1fs time step and total simulation time of 500ps (5000000 steps) at T=298 K. The resulting structure is used in QM (quantum mechanics) calculations by employing Generalized Gradient Approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional / DNP (4.4) basis set + Grimme D-DFT dispersion correction. The optimized structures from GGA/PBE calculations served for the evaluation of the interaction energies and also as initial structures in single point calculations using: DFT/B3LYP-D3/6-311+g(d,p) from which NCI (Non-Covalent Interactions) were plotted.

PSSE P-11

DETERMINATION OF RATE COEFFICIENTS OF CHEMI-IONIZATION PROCESSES

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Not presented.

PSSE P-12

EXAMINATION OF NANOSTRUCTURED CoMoO4 OBTAINED BY GLYCINE NITRATE PROCEDURE

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The synthesis route by solution combustion, a glycine nitrate procedure (GNP) of $CoMoO_4$ nanopowders by a glycine as a fuel and as a complexant was examined concerning the photocatalytic aspects and powder characteristics. The synthesized samples were investigated by differential thermal analysis (DTA), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM) and nitrogen adsorption method. In this work, we presented a simple and effective method for controlling the composition and morphology of $CoMoO_4$. A single-phase α and β crystalline form of $CoMoO_4$ compound was confirmed by X-ray diffraction (XRD). The photocatalytic testing of $CoMoO_4$ nanopowders showed that these nanostructured materials can be promising solutions in photocatalytic processes toward green chemistry and sustainable development.

Keywords: X-ray diffraction, electron microscopy, nanostructured materials.

PSSE P-13

ENERGY LANDSCAPE INVESTIGATIONS OF Y-TERNARY SYSTEM (Y_2O_2S)

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Not presented.

PSSE P-14

LIQUID-LIQUID EQUILIBRIA OF AQUEOUS TWO-PHASE SYSTEMS BASED ON PYRIDINIUM IONIC LIQUIDS

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Ionic liquids (ILs) are the salts with a melting point lower than 373.15 K showing low toxicity, biodegradability, a negligible vapour pressure, high conductivity and thermal stability. In this work phase diagrams for aqueous solutions of twelve new synthesised ionic liquids based on pyridinium cation and chloride or bromide anion combined with K_3PO_4 are reported and discussed. The influence of the polarities of the side chain (n-butyl, 4-hydroxybutyl and a 3-hydroxypropyl) at 1-position in pyridinium ring, as well as the position of the methyl group (ortho, meta or para) on the pyridinium cation, was examined. The binodale curves for the ABS based on the targeted IL were determined via cloud point method [1]. The experimental binodal data were fitted by an empirical Merchuk correlation. The studied pyridinium based ILs with a methyl group in meta and para position show better ability to form ABS comparing to ortho position due to a steric effect that makes a heavy free rotation around single bonds in the side chains for the meta and para position. This effect leads to a significant change in the entropy of the system, which presents the driving forces for the formation of ABS. Ionic liquids with a methyl group in the meta and para position show a similar ability to form an ABS. The presence of a hydroxyl group in the side chain decreases possibility of IL to form ABS due to increasing hydrophilic properties of IL.

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PSSE P-15

A COMPARATIVE STUDY ON THE INTERACTIONS OF IMIDAZOLIUM AND PYRROLIDINIUM-BASED IONIC LIQUIDS WITH ORGANIC CARBONATES

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Experimental densities, electrical conductivities and viscosities for ionic liquids 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide [bmim][NTf_2] and 1-butyl-1-methylpyrrolidinium *bis*(trifluoromethylsulfonyl)imide [bmpyrr][NTf_2] binary mixtures with selected organic acyclic carbonates were measured at atmospheric pressure (p = 0.1 MPa) in the temperature range from T = (293.15 to 323.15) K over the whole composition range. From the experimental density data, the related excess molar volumes were calculated and fitted using Redlich-Kister's polynomial equation. The thermal expansion coefficients were also calculated from the acquired experimental density values. The influence of molecular solvent structure and effects of the carbonates bulky on the nature of interactions and hydrogen bonding in the studied binary mixtures with [bmim][NTf_2] and [bmpyrr][NTf_2] were discussed. Molecular dynamics (MD) and radial distribution functions (RDFs) have been applied to investigate structural properties of the studied system. Based on calculated values for ionicity, potential applications of these mixtures as electrolytes for lithium-ion batteries were examined.

Acknowledgements: Ministry of Education, Science and Technological Development of the Republic of Serbia.

Keywords: ionic liquid, interactions, carbonates, volumetric properties, viscosity, conductivity, lithium ion battery.

PSSE P-16

GRAPHENE OXIDE-$CuFe_2O_4$ NANOCOMPOSITE FOR SIMULTANEOUS ELECTROCHEMICAL DETECTION OF CATECHOL AND HYDROQUINONE

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Catechol (1,2-dihydroxybenzene) and hydroquinone (1,4-dihydroxybenzene) are extensively used in several fields such as textile, dye, petroleum refinery, cosmetics, antioxidant, pesticides and medicines [1]. In the production process, the two isomers can be inadvertently released into the environment as pollutants. These compounds are highly toxic to human health even at very low level [2]. Therefore, a reliable analytical method is needed for the simultaneous detection of catechol and hydroquinone with high sensitivity and selectivity.

This study presents simultaneous determination of catechol and hydroquinone using a new electrochemical sensor based on graphene oxide-$CuFe_2O_4$ nanocomposite. Cyclic voltammetry results show well-defined oxidation and reduction peaks with anodic peaks at 0.35 V for CC and 0.28 V for catechol and cathodic peaks at 0.03 V for CC and -0.08 V for hydroquinone, respectively. A glassy carbon electrode based on graphene oxide-$CuFe_2O_4$nanocomposite showed a proportional change in current response with increasing concentrations of catechol and hydroquinone in 0.1 M PBS, pH 7.4 containing the mixture of catechol and hydroquinone.

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DOI: https://doi.org/10.1016/j.apcatb.2012.09.017.

Keywords: graphene oxide, $CuFe_2O_4$, catechol, hydroquinone, simultaneous detection.

PSSE P-17

GOLD NANOPARTICLE FUNCTIONALIZED GRAPHENE OXIDE NANOCOMPOSITE FILM FOR AMPEROMETRIC DETECTION OF HYDROGEN PEROXIDE

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Graphene oxide, a derivative of graphene, is usually produced by chemical exfoliation of graphite [1]. New combined materials can be prepared with a combination of graphene oxide and metal nanoparticles to improve their existing properties such as catalytic properties, surface-to-volume ratio, surface activity and adsorption ability. The combined materials exhibit highly sensitive and selective response to target substance and also provides the preparation of more effective and robust (bio)sensors [2,3].

This study presents the design of an amperometric sensor for the non-enzymatic detection of hydrogen peroxide. The electrocatalytic activity of graphene oxide-gold nanoparticle nanocomposite towards the electrooxidation of hydrogen peroxide was described by using voltammetric technique. After addition of hydrogen peroxide into 0.1 M PBS, pH 7.4, the cyclic voltammetry results showed an obvious anodic peak at 0.4 V which can be attributed to the oxidation of hydrogen peroxide. The anodic current response of the non-enzymatic sensor increased with increasing the concentration of hydrogen peroxide in 0.1 M PBS, which confirming that graphene oxide-gold nanoparticle nanocomposite indicates a good electrocatalytic activity towards the electrooxidation of hydrogen peroxide.

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Keywords: graphene oxide, gold nanoparticle, hydrogen peroxide, non-enzymatic sensor.

PSSE P-18

MIXED $NH_4Mn_{1-x}Fe_xPO_4 \cdot H_2O$ DITTMARITES AS HIGHLY EFFICIENT PRECURSORS FOR SYNTHESIS OF ELECTROCHEMICALLY ACTIVE $LiMn_{1-x}Fe_xPO_4$ OLIVINES: EFFECT OF THE CATION SUBSTITUTION ON STRUCTURE, IR SPECTRA AND MORPHOLOGY

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Dittmarite-type compounds, $NH_4MPO_4 \cdot H_2O$ (M^{2+} = Mn, Fe, Co, Ni), are a typical example of two-dimensional structure materials with valuable properties like ion-exchange, interlayer ionic mobility, sorption, supercapacitive behaviour and etc.

In the present contribution two main topics have been addressed: (i) To gain a deep understanding of the solid solution formation between $NH_4MnPO_4 \cdot H_2O$ and $NH_4FePO_4 \cdot H_2O$. The choice of just those members of the dittmarite-family is purposeful and it is dictated from the second topic: (ii) To demonstrate the ability of $NH_4Mn_{1-x}Fe_xPO_4 \cdot H_2O$ mixed crystals to act as highly effective precursors for a fast low-temperature synthesis of electrochemically active olivine phase $LiMn_{1-x}Fe_xPO_4$ through an ion-exchange reaction.

The study is focused on the effect of Mn/Fe substitution on the crystal structure, spectroscopic and morphological characteristics of both $NH_4Mn_{1-x}Fe_xPO_4 \cdot H_2O$ and $LiMn_{1-x}Fe_xPO_4$ with emphasizing on the relationship “precursor design − product design”. The different aspects of the cation substitution in the precursors $NH_4Mn_{1-x}Fe_xPO_4 \cdot H_2O$ and target $LiMn_{1-x}Fe_xPO_4$ products such as crystallochemistry, long-range structure, local structure of the $PO_4^{3-}$and Mn^{2+}/Fe^{2+} ions, intermolecular interactions and morphology have been studied by combination of Rietveld analysis based on powder XRD data, IR and EPR spectroscopies and microscopic methods which are highly complementary in describing crystal chemistry of solid solutions.

Based on the precursor $NH_4Mn_{0.8}Fe_{0.2}PO_4 \cdot H_2O$ we have developed a very fast low-temperature method for the preparation of olivine-type $LiMn_{0.8}Fe_{0.2}PO_4$ which is promising electrode material in lithium-ion batteries. The electrochemical activity of a composite material $LiMn_{0.8}Fe_{0.2}PO_4/C$ as a positive electrode in a model two-electrode lithium cell of the type $Li|LiPF_6$ (EC:DMC)$|LiMn_{0.8}Fe_{0.2}PO_4/C$ has been also manifested.

Acknowledgment: The authors are grateful to the financial support from the National Science Fund of Bulgaria (Project DN09/13).

Keywords: solid solutions, Mn/Fe cation substitution, dittmarites, phospho-olivines, intercalation properties.

PSSE P-19

THE PREPARATION OF MESOPOROUS CLAY COMPOSITE CONTAINING DISPERSED IRON OXIDE NANOPARTICLES

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Metal oxides nanoparticles are believed to be capable of exhibiting good catalytic behavior in many heterogeneous catalytic reactions because of their high surface areas and specific surface properties [1]. However, they tend to agglomerate into large particles [2,3]. Therefore, porous materials such as intercalated clay composites may provide high surface areas and easily accessible channels for reaction molecules and benefit their diffusion and catalytic reaction. Here, iron oxide nanoparticles were prepared. Laponite, a type of commercial synthetic hectorite clay, was chosen as the host material. The developed mesoporosity of this clay derivative make that desirable support material for loading other catalytic active compositions.

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Acknowledgements: Research Foundation of Selcuk University (BAP).

Keywords: clay, nanoparticle, catalytic reaction.

PSSE P-20

ZIRCONIA SOL-GEL FILMS, COATED ON SiO_2 AND CeO_2 WITH ENHANCED BARRIER PROPERTIES

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Two types of zirconium dioxide coatings were prepared - one was deposited on SiO_2 and another one – on CeO_2 layers by sol-gel method. The coatings were deposited on stainless steel plates by means of dip coating technique. The morphology and the phase composition were examined by means of Scanning Electron Microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction analyses (XRD). The corrosion resistance of the coatings were examined by evaluation of the weight loss in NaCl medium. The SiO_2/ZrO_2 coatings posess numerous nanosized pores, while the coatings on ceria has a relatively dense, smooth surface. The weight loss measurement have proved that the ZrO_2 on CeO_2 coatings exhibit higher corrosion resistance in comparison to ZrO_2/SiO_2 coatings. After the corrosion attack the coating the surface keep its main characteristics without visible signs of corrosion (pits, craters, etc).

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Keywords: sol-gel, nanosized films, protective properties, films.

PSSE P-21

THE ROLE OF METAL ALKOXIDE ON THE SOL – GEL SYNTHESIS AND PROPERTIES OF Ti AND Zr NANOPOWDERS

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The present investigation deals with comparison of the hydrolysis – condensation behavior of Ti and Zr alkoxides as well as obtaining of corresponding nanopowders. Titanium(IV) butoxide (TBT) and Zr(IV) butoxide (ZBT) with and without addition of solvent (isopropanol) were used during the sol – gel processing. Our previous experience on the sol – gel synthesis of titania powders from titanium(IV) butoxide is applied in this study. In the prepared homogeneous gels the alkoxide/solvent ratio was 1:1 and no water was added during the sol-gel synthesis. The aging of gels was performed in air for several days in order to allow further hydrolysis. By XRD was established that the prepared powdered samples preserved mixed organic - inorganic amorphous structure up to 300°C. By DTA was established that the decomposition of the organics accompanied by strong weight loss occurred in the temperature range 200-300°C. Above 400°C, crystals of TiO_2 (anatase) and ZrO_2 were detected. The average crystallite size (calculated using Sherrer's equation) of the as-prepared powders is about 20 nm. The completness of the hydrolysis – condensation reactions was verified by IR and UV-Vis analyses.

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Keywords: sol-gel; phase transformations; IR spectra; UV-Vis spectra.

PSSE P-22

REDUCED GRAPHENE OXIDE MODIFIED WITH Mg-FERRITE NANOPARTICLES FOR POTENTIAL APPLICATIONS IN BIOSENSORS

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Hydroquinone (HQ, 1,4-dihydroxibenzene) and Catechol (CC, 1,2-dihydroxibenzene) are structural isomers of the dihydroxibenzene species, both widely used in different industrial applications [1] such as coal mining, antioxidants in cosmetics, paint, pharmaceutical preparation, polymers etc. However, these substances are showing high toxic effects to the humans. For example, it was reported that HQ with high concentration could induce headache, fatigue, decomposition, tachycardia, the damage of the kidneys or even death. Decorated graphene and different graphene materials such as graphene oxide (GO), graphene nanoribbons (GNRs), reduced graphene oxide (RGO) found wide application in the field of electrochemistry. These structures showed very promising results as supercapacitors as well as in the field of electroanalytical chemistry for potential application in detection of various samples in different matrices, such as food biological fluids or in the environment.

In this work, facile one step synthesis of magnesium ferrite ($MgFe_2O_4$) nanoparticles decorated on reduced graphene oxide (MgFe@RGO) using a microwave assisted hydrothermal procedure is reported. We used a modification of procedure described elsewhere [2]. The experimental procedure has been altered: 1.75 mmol of $MgSO_4·7H_2O$ and 3.5 mmol of $FeCl_3·6H_2O$ were dissolved in 80 ml distilled water under magnetic stirring and ultrasonic treatment to form a homogeneous solution. Subsequently, 30 wt% of graphene oxide (GO) was added into the above solution under magnetic stirring for 4 h to form a homogenous suspension. The pH value of the suspension was then adjusted to ~10 by adding certain amount of ammonium hydroxide (NH_4OH). The mixture was stirred for 1 h at room temperature. Then, 40 ml of mixture was sealed in a 100-ml microwave Teflon tube and heated at 160 °C for 10 min using a Milestone’s microwave reactor system Ethos Easy and then left to cool to room temperature for further use.

The synthesized material was characterized with help of several techniques and applied for the modification of glassy carbon electrode. Such prepared electrode was utilized for successive simultaneous detection of structurally similar compounds, 1,2- and 1,4-dihydroxibenzenes (catechol (CC) and hydroquinone (HQ)), using differential pulse voltammetry technique (DPV). It was found that oxidation current increases linearly with the concentrations of both investigated compounds. Detection limits for both species are ≤ 0.31 μM. The best analytical response in the presence of both CC and HQ, taking into account peak shape and peak current, was obtained at pH 5.6 utilizing acetate buffer solution. The often-presented species in the surface waters as well as gallic acid and caffeine do not interfere with determination of CC and HQ, while ascorbic acid shows high interference. The method is successfully applied for detection of catechol and hydroquinone in real samples analyses.

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Keywords: MgFe@RGO nanocomposite, magnesium ferrite, dihydroxibenzenes, differential pulse voltammetry

PSSE P-23

PHYSICAL – CHEMICAL CHARACTERIZATION AND ANTIOXIDANT ACTIVITY OF NOBLE METAL NANOPARTICLES FROM *Robinia pseudacacia*

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This research paper describes the phytosynthesis of noble metal nanoparticles, namely silver (AgNPs) and gold (AuNPs) nanoparticles from *Robinia pseudacacia*, a medicinal plant with numerous pharmacological uses. The research focuses especially on the physical – chemical characterization of both plant extract and noble metal nanoparticles using standard techniques such as: qualitative and quantitative screening of phytochemicals, UV-Vis, FTIR, DLS, microscopy, etc.

Keywords: noble metal nanoparticles, physical - chemical characterization, biosynthesis.

PSSE P-24

AMPEROMETRIC DETECTION OF TRIACETONE TRIPEROXIDE AT ELECTRODE MODIFIED WITH GOLD-PRUSSIAN BLUE NANOCOMPOSITE

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Triacetone triperoxide (TATP) is immensely powerful and easy to prepare explosive used in many terrorist attacks in recent years. The absence of nitro groups, no fluorescence, and weak UV absorption makes this explosive very challenging for detection. Using MS or IR spectroscopy is not suitable for on-site testing. Therefore, there is high interest in designing field deployable sensors for detection of TATP that are highly sensitive, small and easy to use. One reported method for detection of TATP is first to irradiate the sample with strong UV radiation after which TATP decomposes to H_2O_2 that is later detected using Prussian blue modified electrodes. [1] Another similar method is based on acid treatment for decomposition of TATP. [2]

The principal idea in our research is to find if presence of gold nanoparticles can facilitate the decomposition of the TATP in acidic media, to H_2O_2 which is then immediately detected using the adjoining Prussian blue nanoparticles as electron-transfer mediator between the electrode and H_2O_2. For the study, a glassy carbon electrode was modified with gold-Prussian blue nanocomposite according to the method by Phani et al. [3] TATP was synthesized, purified and characterized with IR spectroscopy. The sample was then dissolved in 1-propanol. Amperometric measurements were performed at room temperature using a stirred 5 mL solution containing 1-propanol, HCl and 0.1 M KCl as supporting electrolyte. Working potential of 0.0 V versus Ag/AgCl (3 mol/L KCl) reference electrode was applied allowing the transient current to decay to a steady-state value, before spiking a given aliquot explosive solution. Moreover the same experiments were performed with electrode modified with only Prussian blue according to Karyakin et al. [4] The performance of both electrodes is compared.

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Keywords: TATP, amperometric detection, acetone peroxide detection, gold-Prussian blue nanocomposite.

PSSE P-25

SYNTHESIS AND COMPARATIVE STRUCTURAL STUDY OF (2*E*,6*E*)-2,6-BIS[(2-TRIFLUOROMETHYL)BENZYLIDENE]CYCLOHEXANONE AND (2*E*,6*E*)-4-*TERT*-BUTYL-2,6-BIS[(2-TRIFLUOROMETHYL)-BENZYLIDENE]CYCLOHEXANONE

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Curcumin exhibits a wide range of biological activities, such as anti-tumor, anti-inflammation, anti-oxidation, anti-bacterial, and cardiovascular protection. However its practical application is limited due to its high metabolic instability and low bioavailability. Therefore, (2*E*,6*E*)-2,6-Bis[(2-trifluoromethyl)benzylidene]cyclohexanone (fig.1) and (2*E*,6*E*)-4-*tert*-Butyl-2,6-Bis[(2-trifluoromethyl)benzylidene]cyclohexanone (fig.2) were synthesized by aldol condensation of 2-(trifluoromethyl)benzaldehyde and cyclohexanone or 4-*tert*-butylcyclohexan-1-one respectively for the first and the second compound. These compounds are monocarbonyl analogues of curcumin by replacing the β-diketone moiety and show greater metabolic stability than that of curcumin. The compounds were purified by recrystallization and the crystals were powdered for further study. IR spectra of the compounds were recorded using KBr pellets and by using ATR technique. XRPD data was also obtained. By using the obtained data and reference data (the crystal structure only of the first compound is solved [1]), a thorough investigation of the structure of both compounds is performed. Moreover, DFT calculations are done in order to investigate the electron distribution and molecular orbitals in the molecules.

Figure 1. Structure of (2E,6E)-2,6-Bis[(2-trifluoromethyl)benzylidene]cyclohexanone

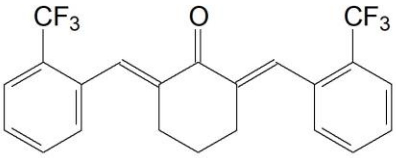
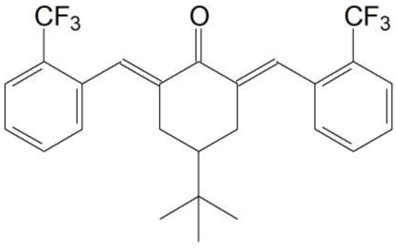


Figure 2. Structure of tert-Butyl-2,6-Bis[(2-trifluoromethyl)benzylidene]cyclohexanone



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PSSE P-26

SYNTHESIS AND CHARACTERIZATION OF PEROVSKITE-MWCNTs COMPOSITES

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Non-stoichiometric perovskites with general formula $Ln_{0.8}Ca_{0.2}Co_{0.5}Cr_{0.5}O_3$ (Ln = Nd or Sm) have been synthesized and then modified with Multi-Walled Carbon Nanotubes (MWCNTs). The characterization of the Perovskite-MWCNTs composites was done by using IR spectroscopy and X-Ray powder diffraction techniques.

The perovskites were synthesized using solution combustion method with glycine as a fuel. The XRD patterns of substituted perovskites showed formation of pure phases. The MWCNTs used in this work were first functionalized by mild acid treatment using mixture of nitric and sulfuric acid [1]. As prepared tubes were modified with perovskites in different perovskite-MWCNTs ratio. Studied composites were prepared by physical modification of MWCTs using ultrasonic bath. In order to investigate the interaction between the tubes and perovskite, the IR spectrum of the pure activated MWCNT was recorded and then compared to the IR spectrum of the composites. Except for the characteristic bands of the MWCNTs and perovskite, in the spectrum of the composites, an evidence of the interaction of the components can be found as well. The band at 1745 cm^{-1} originating from the stretching vibrations of the C=O groups from the MWCNTs, is splitted and can be defined as overlap of three different bands in the spectrum of the composite.

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Keywords: perovskites, MWCNT, XRD, IR spectroscopy.

PSSE P-27

INFRARED AND RAMAN SPECTRA OF $MgRbAsO_4 \cdot 6H_2O$

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Infrared and Raman spectra of the struvite analogue, magnesium rubidium arsenate hexahydrate, $MgRbAsO_4 \cdot 6H_2O$ and of its partially deuterated analogues were recorded from room temperature down to the boiling temperature of liquid nitrogen. According to the crystallographic results, it crystallizes in the orthorhombic space group $Pmn2_1$ with $Z = 2$. $MgRbAsO_4 \cdot 6H_2O$ is isostructural with the biomineral struvite, $MgNH_4PO_4 \cdot 6H_2O$. The existence of strong hydrogen bonds between water molecules is supported by the appearance of a broad band from 3800 to 2200 cm^{-1} in the stretching region of the vibrational spectrum. In the HOH bending region in the IR spectra, one complex band appears with more distinctive maxima. Several bands can be seen between 1000 and 400 cm^{-1}in the vibrational spectra. On the basis of a careful analysis of the vibrational spectra of the protiated compound, as well as those of its partially deuterated analogues, in the infrared and Raman spectra of almost completely deuterated analogue, we assigned the band at around 815 cm^{-1} to the $\nu_3(AsO_4)$ mode and that at around 820 cm^{-1} to the $\nu_1(AsO_4)$. In the LNT infrared spectrum the bands with a low intensity at around 470 and 445 cm^{-1} were assigned to the $\nu_4(AsO_4)$ bending vibration. The remaining bands are assigned as due to librational and translational modes of the water molecules.

Keywords: magnesium rubidium arsenate hexahydrate, infrared spectra, Raman spectra.

PSSE P-28

$Mg_2KH(XO_4)_2·15H_2O$ (X = P, As) CONTAINING ACIDIC DIMER UNITS: ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY, IR SPECTROSCOPY AND DSC STUDIES

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The electrical properties of little known compounds of the type $Mg_2KH(XO_4)_2·15H_2O$ (X = P, As), their dc and ac conductivity and complex impedances are studied for the first time by Electrochemical Impedance Spectroscopy in narrow temperature interval from room temperature until 76 °C. These compounds present interesting electrical behavior with change of the conductivity mechanism and sharp increase in conductivity to $\sim 10^{-2}$ S m^{-1} when subjected to thermal treatment without structural changes. The complex impedance plots confirm the contribution of two relaxation mechanisms, through grains and grain boundaries, the later becoming dominant at higher temperatures. The ac conductivity obeys Jonscher's power law and is in good agreement with the correlated barrier hopping model. In order to explain their conductivity behavior, the salts are additionally studied by differential scanning calorimetry (DSC), infrared and attenuated total reflectance spectroscopy at higher temperatures.

Keywords: $Mg_2KH(PO_4)_2·15H_2O$, $Mg_2KH(AsO_4)_2·15H_2O$, ionic conductors, conduction mechanism.

Biotechnology and Food Technology (BFT)

BFT O-1

PRODUCTION OF ENZYMES BY A NEW STRAIN STREPTOMYCES FLUVISSIMUS CKS7 USING AGRICULTURAL BY-PRODUCTS

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In recent years, there have been an incresaing interest for reuse of agricultural by-products expecially in the field of microbial enzymes production. Theese kind of a agricultural waste are abundant, cheep and represent a good source of fermentable sugars and proteins which are necessary for microorganisms growth and enzymes production. Because of the stil high price of commercial enzymes, microbial enzymes produced by this way could reduce the cost of entire process.

The potential of a novel bacterial strain *Streptomyces fluvissimus* CKS7, previously isolated from a soil, to produce industrially important enzymes was evaluated using selective agar plates. The strain was able to produce extracellular cellulase (CMC-ase and Avicelase), amylase, pectinase and xylanase.

Different types of agricultural by-products (wheat bran, barley bran, ray bran, sunflower meal and soy meal) were used as substrates for CKS 7 growth and enzymes production. Solid state fermentation (SSF) was performed using these waste substrates. Among tested agricultural by-products, ray bran showed maximum enzymes production. During SSF on rye bran, the strain CKS7 produced several enzymes: cellulase (Avicelase and CMC-ase), amylase, pectinase and xylanase. An optimum solid: moisture ratio for maximum enzymes production was investigated. Maximum of CMC-ase 2.81 U/g, Avicelase 2.67 U/g, amylase 7.63 U/g, xylanase 6.84 U/g and pectinase 9.81 U/g activity was obtained at the sixt day of incubation with 10% of inoculum using rye bran as substrate. The results obtained in this study showed that agricultural by-products could be used as substrate for enzymes production.

Keywords: agricultural by-products, SSF, microbial enzymes, *Streptomyces fluvissimus* CKS7.

BFT O-2

THE EFFECT OF EDIBLE COATING CONTAINING TURKISH MOUNTAIN TEA EXTRACT ON THE FRESH STRAWBERRIES

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Strawberries are highly perishable fruits that are inclined to mechanical injury, dehydration, and decay during the storage period. This study aimed to increase the shelf life of strawberries by coating with the whey protein edible coating containing the ethanolic extract of mountain tea. Mountain tea (*Sideritis* spp.) was chosen because of the biological effects such as antimicrobial and antioxidant activity. This plant is grown especially in the Mediterranean region of Turkey. For the purpose, ultrasound-assisted ethanolic (70%) extraction was performed and used to prepare whey protein coating solution. The total phenolic compound was determined as 7152 mg GAE/100 g by using Folin-Ciocalteu assay. Antioxidant activity of the extract was also identified as percentage inhibition of DPPH concentration. The IC (%) of extract was found as 36.66%. Whey protein coating solution (10 g/100 ml) was prepared with the 10% mountain tea extract. Strawberries were then dipped to this solution and stored for 14 days at 4 °C. During the shelf-life period, the number of the total aerobic mesophilic bacteria (TAMB), yeasts and molds and the visual decay of strawberries were examined. The TAMB were counted as 0.98, 2.33 and 3.77 log cfu/ml at the day 0., 7. and 14. While the total count of yeasts and molds were 1.28, 2.65 and 3.91 log cfu/ml respectively. To observe the decay of strawberries, the percentage of lost fruits during the 14 days of storage were determined. At the end of the 10th day, 100% of uncoated fruits were deteriorated, whereas the decay level was 30% at the same day and 77% at the end of the storage period (14th day). It is obvious that, the coating of fruits inhibits the microbiological growth. It can be concluded, the whey protein coating solution incorporated with mountain tea extract has the ability to extend the shelf life of fresh strawberries.

Keywords: edible coating, whey protein, mountain tea extract, strawberries.

BFT O-3

EXTRACTION OF TOTAL CAROTENOIDS AND β-CAROTENE FROM PUMPKIN BY USING DIFFERENT SOLVENT SYSTEMS

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Food and food products contain lots of carotenoid content which responsible for reducing the risk of neurodegenerative such as cancer and cardiovascular diseases. Carotenoid is a pigment naturally present in pumpkin and also gives the orange color. It is aimed in this study to improve the extraction efficiency of beta carotene from pumpkin by using different solvents systems.

In our study, β-carotene was extracted from pumpkin using 5 different solvent system with different polarity. Solvent compositions were acetone:petroleum ether (1:1), ethanol (100%), acetone (100%), acetone:ethanol:hexane (1:1:2) and methanol:ethyl acetate (6:4). Butylated hydroxytoluene was added to all extracts to prevent oxidation. The total carotenoid content of the extracts was determined by spectrophotometrically. The β-carotene content was measured with HPLC method. Total carotenoid contents of the extracts were found between 34.44-39.72 µg/g. ß-carotene content of the extracts was determined as 22.85-46.14 µg/g. The highest total carotenoid and ß-carotene content were found for methanol:ethyl acetate (6:4) extract.

Besides the carotenoid analysis, color analysis of these extract was made by using Lovibond tintometer and color differences of the extracts in terms of ß-carotene content were compared. L values of the extracts were determined between 72.65-99.92; a* values were determined as -3.74-7.19; while b* values were determined as 0.06-131.28.

The results showed that carotenoid content differs depending on the extraction method. The polarity of the solvents which used for the extraction affects the total carotenoid and ß-carotene content. It can also conclude that nonpolar solvents are more effective in extracting ß-carotene.

Keywords: beta carotene, extraction, total carotenoid.

BFT P-1

POSSIBILITY OF USING MICROBIAL ENZYMES PRODUCED BY *Streptomyces fluvissimus* CKS7 IN HYDROLYSIS PROCESS

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The microbial enzymes are biological catalysts that perform reactions in bio-processes in an economical and environmentally-friendly way as opposed to the use of chemical catalysts. Microbial enzymes, obtained by different microorganisms are of great importance for application in industrial bioprocesses [1,2]. The use of microbial enzymes in various industries (e.g., food, agriculture, chemicals, and pharmaceuticals) is increasing rapidly due to reduced processing time, low energy input, cost effectiveness, nontoxic and eco-friendly characteristics [3]. Cellulase are the largest group of industrially important enzymes with a potential to convert cellulose into fermentable sugars [4]. Amylases represents a second largest group of industrial enzymes which are used for the degradation of starch to glucose, maltose, dextrins…[5]. Xylanase are important for pentose production, fruit juice clarification…while pectinase degrade pectic substances in the cell wall of higher plants.They are important in food-processing industries, mainly for extraction and clarification of fruit juices and wines, extraction of tomato pulp, oil extraction, and tea and chocolate fermentation [1,2]. All these enzymes (cellulase, amylase, xylanase and pectinase) could be used for agro-industrial residues utilization that lead to bioethanol production.

In this study a crude “enzymes cocktail” that produce *Streptomyces fluvissimus* CKS7 was used in a hydrolysis process of different lignocellulosic waste materials. The strain CKS7 produced cellulase (CMC-ase and Avicelase), amylase, pectinase and xylanase during solid state fermentation (SSF) on agricultural by-product – rye bran. Obtained crude enzymes were used for hydrolysis of different lignocellulosic substrates: corn stalk waste, *Equisetum arvense* waste, *Gentiana lutea* waste, cotton fabric and corona treated cotton fabric. Released reducing sugars was measured during 3 days of hydrolysis at 50 °C. The results revealed that the concentration of reducing sugars was increasing during hydrolysis in all tested lignocellulosic substrates. Although the concentration of released reducing sugars are relatively low (~ 1.9 mg/ml) in all tested samples, this is the first study that deals with enzymatic potential of the *S. fluvissimus*. Further experiments should be focused on optimization of enzymatic hydrolysis of lignocellulosic substrates.

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Keywords: microbial enzymes, Streptomyces fluvissimus CKS7, lignocellulosic substrte, hydrolysis.

BFT P-2

DETERMINATION OF CAPSAICIN CONTENT AND ANTIOXIDANT ACTIVITY OF HOT PEPPER (*Capsicum annuum* L.) SEEDS ETHANOLIC EXTRACT

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Hot peppers (*Capsicum annuum* L., Solanaceae) are used worldwide because of the color, pungency and aroma of their fruits. Pepper fruits could be eaten fresh, cooked, powdered or processed into oleoresins. As an excellent source of natural colors and antioxidant compounds peppers also have their nutritional value. The color of paprika fruits is attributed to the carotenoids formed during ripening with capsanthin as the main one, followed by capsorubin and provitamin A carotenoids. On the other side, pungency depends on the presence of capsaicinoid group of compounds such as capsaicin, dihydrocapsaicin, norcapsaicin, nordihydrocapsaicin, homocapsaicin and homodihydrocapsaicin. Capsaicin, as the most abundant capsainoid (making about 71% of the total capsainoids) is the active principle that bears responsibility for pharmaceutical properties of peppers. It is used as an analgesic for arthritis pain and inflammation, showing anticancer effects as well as protective effects against cholesterol and obesity.

The aim of the present work was to determine antioxidant activity of hot peppers seeds ethanolic extract as well as its capsaicin content. Ethanolic extract was obtained by Soxhlet extraction during 2h. One part was then concentrated in vacuum using rotary evaporator, at temperature bellow 60°C and filtered through 0.45μm filter before the analysis. Qualitative and quantitative composition of capsaicin in the concentrated extract was determined by HPLC chromatography using gradient elution regime with formic acid (0.1% water solution) (eluent A) and acetonitrile (eluent B) as mobile phase. Capsaicin was quantified using the calibration curve built by injecting ten increasing concentrations (0.006-1 mg/ml) of capsaicin standard. Antioxidant activity on stable DPPH (1,1-diphenyl-2-picrylhydrazyl) radical was determined spectrophotometrically, applying DPPH assay, after 20 min and 40 min incubation with radical.

The content of total extractive matter was 5.27 g/100 g of plant material. Capsaicin content was determined to be 0.618 g/100 g of dry extract i.e. 0.0326 g/100 g of plant material. The degree of DPPH radical neutralization depends on the extract concentration and incubation time applied. Better antioxidant activity showed extract incubated for 40 minutes. Concentrations of extract needed for 50% of initial DPPH radical concentration neutralization were 0.666 mg/ml (after 20 minutes) and 0.656 mg/ml (after 40 minutes incubation with radical).

The results presented showed that the isolated hot peppers ethanolic extract is a potential source of natural antioxidants.

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Keywords: hot pepper, *Capsicum annuum* L., HPLC analysis, antioxidant activity.

BFT P-3

COMPARATIVE ANALISYS OF CHEMICAL COMPOSITION AND ANTIOXIDANT ACTIVITY OF ISOLATED AND COMERCIAL ESSENTIAL OIL FROM ROSEMARY (*Rosmarinus oficinalis* L.)

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Rosemary (*Rosmarinus officinalis* L.) is a perennial plant belonging to the family of Labiatae (Lamiaceae). Rosemary leaves contain approximately 2% of essential oil exhibiting analgesic, antispasmolytic, adstringent, antioxidant and antimicrobial effects. The most abundant compounds in rosemary essential oil are 1.8-cineole, α-pinene and camphor. The aim of this work was comparative study of chemical composition and antioxidant activity of isolated (Institute of Medicinal Plants Research "Dr Josif Pancic", Belgrade) and comercial (MeiLab, Belgrade) essential oil from rosemary (*Rosmarinus oficinalis* L.).

The essential oil from ground rosemary leaves was isolated by conventional hydrodistillation using hydromodule of 1:15 m/v during 120 minutes. Qualitative and quantitative composition of the isolated and commercial essential oil was determined by GC-MS and GC-FID analysis. The antioxidative activity of rosemary essential oils was investigated by DPPH assay in terms of their possible application as natural antioxidants.

The yield of isolated essential oil was 1.57 ml/100 g of plant material. It was identified 84.59% and 99.39% of total oil composition in isolated and commercial essential oil, respectively. Qualitative and quantitative composition of oils was different. The major compounds in the isolated rosemary essential oil were camphor (17.75%), borneol (13.5%) and verbenone (24.27%), while the most abundant compounds in the commercial oil were: 1,8-cineole (43.92%), camphor (10.65%) and α-pinene (13.19%). The isolated essential oil showed better antioxidant activity for all incubation times (20 min, 40 min, 60 min, 90 min and 120 minutes of incubation). The reason lies in the fact that two investigated oils have different chemical composition. The best antioxidant activity showed isolated essential oil after 120 min of incubation (EC_{50}=13.79 mg/ml).

The obtained results regarding the antioxidant activity of essential oil isolated from rosemary leaves indicate its possible application in food and pharmaceutical industry as safer alternative to synthetic antioxidants.

Acknowledgements: This work is part of the research project "Plant and synthetic bioactive products of new generation," no. TR 34012, financed by the Ministry of Education, Science and Technological Development of Republic of Serbia.

Keywords: *Rosmarinus officinalis* L., essential oil, GC/MS analysis, antioxidant activity.

BFT P-4

ANTIOXIDANT ACTIVITY OF AQUEOUS EXTRACT FROM RASPBERRY (*Rubus idaeus* L.) LEAVES ESIMATED BY DPPH TEST

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Raspberry (*Rubus idaeus* L.) is one of many perennial deciduous plants with perennial root and with one- or two-year sprouts. It is a member of *Rosaceae* family, and the red raspberry variety is a commercially grown berries. The most important compounds, which have been found in raspberry, included phenols and sesquiterpenes, aldehydes and ketones, aliphatic and aromatic hydrocarbons, C13-norisoprenoids. Leaf of raspberry has high content of magnesium, calcium, iron, potassium, vitamin C and B-vitamins and it has been known as very beneficial healing herbs.

Dried plant material was subjected to extraction in water using two extraction techniques – maceration at 25ºC and reflux at boiling temperature. The hydromodulus was 1:20 m/v and extraction was performed 120 minutes.

The qualitative content of obtained extracts has been investigated by LC-MS chromatography in order to determine phenolic compounds represented in the highest percentage. The most represented compounds in the extracts were quercetin-3-glucuronide and kaempferol-3-glucuronide.

Antioxidant activity of obtained extracts has been investigated by DPPH test based on the electrons exchanging between an antioxidant and stable DPPH radical resulting in colour of the reaction mixture changing. The bleaching of the reaction mixture is quantitatively monitored by absorbance at 517 nm monitoring, on the basis of which the percentage of DPPH radical neutralization is calculated. DPPH test is performed immediately after reagents mixing and after 20 min of incubation. The total extractive matters were 17.6 and 27.5 g/100 g of plant material for maceration and reflux extraction, respectively. Obtained EC_{50} values were 0.045 mg/ml (reflux extraction) and 0.13 mg/ml (maceration); after incubation, the EC_{50} values were 0.018 mg/ml and 0.029 mg/ml for reflux and maceration extraction, respectively. The extracts obtained by reflux extraction have shown higher antioxidant activity in both cases which means that phenolic compounds extracted in higher yield are responsible for the antioxidant activity. The phenolic compounds extracted on this way will be used as stabilizing and reducing agents in further production of metal-nanoparticles (silver and gold) as a base of cosmetic products for topical application.

Acknowledgements: This work is part of the research project "Plant and synthetic bioactive products of new generation," no. TR 34012, financed by the Ministry of Education, Science and Technological Development of Republic of Serbia.

Keywords: raspberry leaves, aqueous extracts, LC-MS chromatography, antioxidant activity, DPPH test.

BFT P-5

THE GROWTH OF *Enterococcus faecalis* MK3-10A ON THE COMBINED MEDIA WITH GLUCOSE AND WASTE GLYCEROL

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The possibility of microbial utilization of combined glucose and waste glycerol by lactic acid bacteria *Enterococcus faecalis* MK3-10A on laboratory level was studied. Waste glycerol from biodiesel production is a valuable raw material that can be used for production of valuable microbial metabolites, especially if it is combined with some commercial carbon source. Previous researches [1, 2] have shown that the combined sources of carbon have a stimulative effect on the primary and secondary microbial metabolism.

The *E. faecalis* bacteria was grown at 28 ºC under static conditions (without shaking) in the MRS (de Man, Rogosa, Sharpe) broth (pH 6,4) (Torlak, Belgrade) with a mixture of glucose and either pure glycerol or waste glycerol obtained as a by-product from the biodiesel production from sunflower and rapeseed oil. The strain *E. faecalis* MK3-10A was isolated from a seven-month-old cream (kaymak) sample [3]. Microbial growth (OD_{620}) was measured spectrophotometrically at λ = 620 nm, using a Cole Parmer 2100 UV/VIS spectrophotometer, whereas the concentration of lactic acid was determined using the HPLC method.

The bacterium *E. faecalis* MK3-10A showed the best growth ($OD_{max} = 0.690$) and the highest productivity (13.9 mg/mL/d) in the medium containing the mixture of pure glycerol and glucose as a carbon source. A slightly lower value (8% and 5%) was achieved in the medium with glucose and waste glycerol from sunflower oil. The lowest growth ($OD_{max} = 0.478$) and the lowest productivity of lactic acid (10.41 mg/mL/d) were obtained during the growth in the medium with glucose and waste glycerol from rapeseed oil.

Therefore, waste glycerol from the production of biodiesel from sunflower oil can be considered a promising cheap carbon source for further research on the possibility of lactic acid bacteria cultivation for producing lactic acid.

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Keywords: actic acid bacteria Enterococcus faecalis MK3-10A, waste glycerol.

BFT P-6

UTILIZATION OF WASTE GLYCEROL FROM BIODIESEL PRODUCTION BY FRESHWATER MICROALGAE

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Algae are an inexhaustible source of inspiration and research ideas. Because of their great diversity, diversity of biochemical composition of biomass and metabolic pathways, the extraordinary genetic potential, and adaptability, algae reveal still unknown and extraordinary limits and possibilities of solution finding for many global problems [1]. In recent years, special attention has been given to the ability of algae to store energy in form of oil, which is an interesting and sustainable raw material for biodiesel production. Also, many studies of the utilization of waste glycerol by microalgae have been published [2, 3]. These studies show that some strains of freshwater microalgae can produce lots of important products by fermenting waste glycerol from biodiesel production. In recent years, the supply of waste glycerol has drastically increased because of the increase of biodiesel production.

The aim of this work was to study the effect of waste glycerol, obtained from the biodiesel production from sunflower and rapeseed oils on the production of oil using freshwater microalgae, which were isolated from the South Serbian stagnant water samples.

In this study, two isolated microalgae strains identified as members of the *Chlorococcum* and *Chlorella* genera were used. The strains were isolated from the Leskovac area swamps in the Laboratory for Microbiology and Food Technology, the Faculty of Technology, Leskovac in 2012. The strains were cultivated in 1000 mL Erlenmeyer flasks in the liquid Bolds Basal Medium (BBM) (pH 6,6) at 22 ^{o}C under the constant light for 30 days at an orbital shaker (140 min^{-1}). Pure and waste glycerol was added to the medium in an amount of 15 g/L. The waste glycerol from sunflower and rapeseed oil was obtained from the Laboratory for Chemical Engineering, the Faculty of Technology, Leskovac. The dry biomass concentration was measured after the algae entered in the stationary growth phase. The change in the concentration of glycerol was determined by the HPLC method. The content of algal oil was determined gravimetrically, after extraction from dry biomass by the Bligh-Dayer method using chloroform and methanol (2:1 v/v). The results obtained under these cultivation conditions were compared with the results obtained by the autotrophic cultivation of algae.

As opposed to the original medium and the medium with pure glycerol, the isolated algae strains of the genus *Chlorella* and *Chlorococcum* showed a lower growth in the media with waste glycerol, especially in the medium with waste glycerol from rapeseed oil. In the medium with waste glycerol from rapeseed oil, the *Chlorella* and *Chlorococcum* strains reached the dry biomass value of 0.7 g/L and 1.3 g/L, respectively. The highest value of dry biomass (1.7 g/L) was achieved with the *Chlorococcum* strain in the medium with pure glycerol. Compared to the preliminary conducted autotrophic cultivation, a 9% lower value (1.1 g/L) was obtained with *Chlorella* strain in the pure glycerol medium. During the studied process, *Chlorella* sp. consumed 51% of pure glycerol, while *Chlorococcum* sp. consumed all the available amount of pure and waste glycerol from sunflower oil. In the medium with rapeseed oil, despite the low growth, the *Chlorococcum* strain produced the highest oil yield, 23% of dry biomass. Growing in the medium with waste glycerol from sunflower oil, *Chlorella* sp. produced the highest achieved oil yield, 35% based on dry biomass.

In general, the addition of waste glycerol from biodiesel production to the algal medium had a slightly inhibitory effect on algae but a stimulation effect on the oil production. Therefore, waste glycerol, especially from sunflower oil, can be considered as a significant and promising source of carbon for further research with algae.

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Keywords: freshwater microalgae, waste glycerol.

BFT P-7

MINERAL COMPOSITION AND PHENOLIC CONTENT OF POMEGRANATE FRUIT (*Punica granatum* L.)

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Along with olives, figs and grapes, pomegranates are among the first plants to have been cultivated by man. The popularity of pomegranate is increasing among growers and consumers due to its nutritional value, nutraceutical properties and adaptability to different soils and climate conditions. In this study, mineral composition and total phenolic content in seven pomegranate cultivars produced in Republic of Macedonia (Lifanka, Bejnarija, Karamustafa, Ropkavac, Valandovska kisela, Zumnarija and Hicaz) were determined besides other chemical properties. The results obtained showed significant differences among varieties. In order to establish the mineral composition, twenty three elements were quantified in fresh and dried aril. The analyses were performed using inductively coupled plasma – atomic emission spectrometry (ICP-AAS) method. The amount of some elements, such as Ag, As, Bi, Cd, Co, Cr, Li, Mo, Ni, Pb, Tl and V, were below the detection limit. Yet, the rest eleven elements showed wide range in the amounts between the investigated pomegranate varieties, both in fresh and dried aril. According to the results obtained, pomegranate can be considered as a good source for minerals such as calcium (96-372 mg/kg), iron (4.33-8.40 mg/kg) and magnesium (164-431 mg/kg), potassium (2111-5558 mg/kg) and sodium (8.4-20.9 mg/kg).

Pomegranate, also, has been described as a rich source of (poly)phenolic components, with a broad array of different structures. In this study, beside the elemental characteristics (pH, total soluble solids, sugars, titratable acidity), a quick screening for phenols, anthocyanins and catehins was performed. The results obtained indicated that pomegranate can be considered as very rich source for phenolic compounds and strong antioxidant activity.

Keywords: pomegranate, micro and macro elements, phenolic composition.

BFT P-8

IN VITRO ENZYMATIC DIGESTION OF GLUCOSINOLATES AND ISOTHIOCYANATES OF *Lepidium latifolium* L.

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Lepidium is a genus of plants in the mustard family Brassicaceae, native to southern Europe, Mediterranean countries and Asia. This family is strikingly characterized by glucosinolates (GLs) as molecular tags which breakdown products, isothiocyanates are known to possess various biological activities [1]. *Lepidium latifolium* L. (perennial pepperweed) has been extensively used in traditional medicine for over 2000 years. In France, known as the Plant of Maylis, it is traditionally cultivated by monks in their gardens of medicinal plants since the ninth century, where today it is produced in two forms: depurative tea, and capsules of food supplements [2]. It is also one of the preferred phytofoods in the cold arid region of Ladakh (India), contributing significantly to people’s diet in that area of the Himalayas [3].

In this study, the gastrointestinal stability of GLs, extracted from leaves of *L. latifolioum* was investigated. GLs were characterized indirectly by GC-MS using their breakdown products, mostly isothiocyanates (ITCs). The main GL was sinigrin, accompanied by glucotropaeolin. Extracted GL fractions and pure sinigrin, as well as allyl ITC (sinigrin degradation product), and benzyl ITC (glucotropaeolin degradation product) were submitted to a two-phase *in vitro*digestion process using human gastrointestinal enzymes. In addition, the effect of pH (2.5 and 7.5) on GLs and ITCs stability was investigated. Quantifications of the investigated GLs were carried out by HPLC analysis of desulfoglucosinolates, while ITCs were quantified by GC-FID. The *in vitro* digestion showed the instability of sinigrin during duodenal digestion. The allyl ITC and benzyl ITC showed to be stable during digestion process and acidic pH, while it showed to be very unstable on pH 7.5.

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Acknowledgements: The research was funded by Croatian Science Foundations (Grant IP-2016-06-1316).

Keywords: glucosinolates, isothiocyanates, sinigrin, in vitro digestion.

BFT P-9

INDUSTRIAL PRODUCTION OF BEATEN CHEESE WITH PROPIONIC BACTERIA

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Following the growing interest in traditional dairy products from the Balkan Peninsula in the European Union countries, this study focused on the industrial production of beaten cheese with propionic bacteria in order to achieve characteristics of traditionally produced beaten cheese.

Three varieties of beaten cheese were produced industrially from pasteurized cow's milk. The first type (PC) was prepared with the starter culture F-DVS YF-3331 YO-Flex (lactic acid bacteria *Lactobacillus delbrueckii* subsp. *bulgaricus* and *Streptococcus thermophilus*). The second variant (C1) was produced with the starter culture FD-DVS XPL-1 (lactic acid bacteria *Lactocossus lactis* subsp. *cremoris*, *Lactococcus lactis* subsp. *lactis biovar diacetylactis*, *Lactococcus lactis* subsp. *lactis*, *Leuconostoc* and *Streptococcus thermophilus*), while for the third variant (C2) beside the primary starter culture FD-DVS XPL-1, a secondary starter culture FD-DVS PS-4 (propionic bacterium *Propionibacterium freudenreichii* subsp. *shermanii*) was used, also.

The chemical and sensory characteristics of all cheese varieties were evaluated during the ripening period of 45 days. The industrially produced beaten cheese varieties were compared with cow's beaten cheese traditionally produced (TP) from unpasteurized milk. The chemical content of the cheese samples was calculated according to the dry matter content. The sensory analysis was carried out with 17 panelists.

After 45 days of ripening, the dry matter for the beaten cheeses was 74.98% for PC, 57.64% for C1 and 56.26% for C2, while TP had dry matter of 53.9%. The fat content was 31.81%, 37.91%, 40.69% and 40.0%, while the protein content was 43.97%, 50.57%, 50.76% and 35.53% for PC, C1, C2 and TP, respectively. The salt content was 4.80% for PC, 5.46% for C1, 4.09% for C2 and 4.17% for TP. The pH value and water activity ranged from 4.70, 4.95, 4.65 to 5.14, and from 0.72, 0.73, 0.76 to 0.80 for PC, C1, C2 and TP, respectively. The overall sensorial acceptance was 4.24, 4.11, 6.17 and 5.64 for PC, C1, C2 and TP. The C2 variety resembled the most the traditionally produced beaten cheese.

Keywords: beaten cheese, industrial production, traditional production, propionic bacteria, quality characteristics.

BFT P-10

EXTRACTION OF WILD OREGANO WITH DIFFERENT PARTICLE SIZE

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Nowadays, due to the wide range of bioactivities, the isolated plant compounds are exceptionally interesting high-value ingredients for applications in food and pharmaceutical industry, as well as, cosmetology and agriculture [1,2]. During extraction processes, highly significant is to study and optimize the effects of the working conditions to obtain higher extract yields and bigger content of bioactive compounds in the extracts [3].

The effect of the particle size at extraction of the wild oregano (*Oreganum minutiflorum*) cultivated in the Republic of Macedonia was investigated in this study. The wild oregano with 0.25 mm, 0.5 mm and 1 mm particle size was extracted by using *Soxhlet* method and 96 *v/v*% ethanol as a solvent at 1:30 *w/v* solid-to-liquid phase ratio for 180 min. The extract quantity and chlorophyll content in the extracts were followed during extraction. The samples of wild oregano before and after extraction were evaluated according to the parameters obtained by analysis of surface color (L^*, a^*, b^*, C and Ho) and thermogravimetric analysis (TGA/DTA).

The effect of the wild oregano particle size, on the extract yield and content of chlorophyll in it, is significant. The highest extract quantity (16.4 g/100 g dry sample) was obtained at the extraction of wild oregano with 1 mm particle size. The quantity of total chlorophylls in the extracts increases with decreased particle size from 1 mm to 0.25 mm, which is in agreement with the determined values of the color parameter a^*. The color saturation (C) and hue angle (Ho), on the other hand, decrease with the increase of particle size. TGA/DTA analysis has shown that oregano particles of lower size have higher thermal stability. The thermal destruction for 1.0 mm oregano particles starts around 200ºC while for 0.25 mm the thermal destruction temperatures were shifted to 230ºC.

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Keywords: wild oregano, particle size, extract, color and TGA/DTA parameters.

BFT P-11

MODELING *Bacillus subtilis* GROWTH KINETICS UNDER DIFFERENT OXYGEN TRANSFER RATES

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Bacillus subtilis has industrial significance as a growth promotor in plants and represents a potential component of microbial fertilizers which are alternative to chemical fertilizers that are polluting the environment. In order to produce an effective formulation, fermentation process should be understood and optimized to give a maximum number of viable cells. The aim of this study was to develop a model to describe the growth kinetics of *B. subtilis*, as well as to determine the influence of different oxygen transfer rates (OTR) on *B. subtilis* growth. Culture was grown in Erlenmeyer shake flasks, filled with different medium volume, on a rotary shaker at a constant temperature of 31 °C and agitation speed of 150 rpm for 72 h. Samples were taken at regular intervals to determine the number of viable cells using the spread plate method. Oxygen transfer rate was determined using the empirical equation given by Veljković et. al. (1995). Data analysis was performed using IPMP 2013, a free predictive microbiology software tool developed by the USDA ARS. Culters grown on the higher OTR showed higher specific growth rate (0,328 h^{-1}) when compared to the cultures grown on the lower OTR (0,209 h^{-1}). A maximum number of viable cells ($2.2 \cdot 10^9$ CFU/ml) was achieved after 60h of cultivation at the highest OTR value examined. Growth curves represented full growth with a lag, exponential and stationary growth phase which allowed the application of Huang full growth model, with root mean squared error lower than 0,01 in both cases. Average cell number given by Huang model was 9.176 and 9.082 log CFU/ml for the cultures grown in medium with the highest and the lowest OTR, respectively. To determine the accuracy of the model, the next step of the study will be model validation and compartment to other models available.

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Keywords: *Bacillus subtilis*, OTR, modeling.

BFT P-12

ANTIOXIDANT AND ANTIMICROBIAL ACTIVITY OF PLOVDINA WINE WITH AROMATIC PLANTS

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The effects of the addition of aromatic herbs on the antioxidant and antimicrobial activity of the Plovdina red wine were studied. Aromatics herbs: anise seeds (*Pimpinella anisum* L.), cinnamon bark (*Cinnamomum zeylanicum*), wormwood leaf (*Artemisia absinthium*) and licorice root (*Glycyrrhiza glabra*) were added (1% w/w) to Plovdina pomace at the beginning of fermentation.

The highest antioxidant activity was observed in Plovdina wine with cinnamon (EC_{50} = 0.023±0.001 mg/ml), whereas the lowest antioxidant activity was observed in Plovdina wine (control sample), EC_{50} = 0.067±0.0006 mg/ml. All the analyzed wine samples express antimicrobial activity against G(+) bacteria *Bacillus subtilis*. However, they didn't show activity against Gram(-) bacteria: *Escherichia coli*, *Salmonella typhimurium* or *Candida albicans* yeast.

Acknowledgements: Ministry of Education, Science and Technological Development.

Keywords: wine, Plovdina, antioxidant, antimicrobial.

BFT P-13

IRREVERSIBLE Bacteriopheophytin *a* DEGRADATION INDUCED BY VISIBLE LIGHT, UV-A AND UV-B IRRADIATION IN METHANOL SOLUTIONS

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The red and the purple photosynthetic bacteria contain a very important "chlorophyll-type" pigment - bacteriochlorophyll (BChl). A major distinction among the various classes of chlorophylls which defines very characteristic spectral features is the degree of unsaturation of the porphyrin macrocycle. Bacteriochlorin macrocycle is a 7,8-*trans*,17,18-*trans*-tetrahydrophytoporphyrin system, found in BChl *a*, *b* and *g* of anoxygenic bacteria. On the other hand, bacteriopheophytin *a* (BPheo*a*) is a structurally similar compound to BChl*a*, and it is differs only in absence of central metal magnesium (Mg). Lack of Mg from the porphyrin macrocycle system in BPheo*a* may lead to significant differences in its UV-VIS absorption and photostability, in comparison to BChl*a*. BPheo*a* can be used in a various fields, such as anti-cancer *Photodynamic Therapy* in medicine, due to its photosensitive properties during UV and VIS absorption. Therefore, it is very important to determine BPheo*a* photostability against different irradiation treatments.

The degradation of BPheo*a* during VIS, UV-A and UV-B irradiation treatments in the methanol solutions, has been studied by absorption UV-VIS spectroscopy, by using Q_y absorption band as sensible indicator of detected changes and for kinetic analysis. Continuous UV irradiation of BPheo*a* solutions was performed in cylindrical photochemical reactor "Rayonet", equipped by ten symmetrically placed Hg-lamps, with emission maxima in two different UV sub-ranges, UV-A (350 nm) and UV-B (300 nm) and total measured energy flux 12.9 W m^{-2} and 15 W m^{-2}, respectively, at 10 cm distance. Continuous illumination of BPheo*a* solution with VIS light (200-800 nm), was performed in hand-made cylindrical photochemical reactor equipped with symmetrically placed LED lamps at 10 cm distance from the samples (number of LED lamps was 60 com./m, distance between lamps 16 mm, light color "Pure White", emitting angle 120° spherical). The total measured energy flux received by the samples was 14 W m^{-2}. Absorption UV-VIS analyses were done on a Varian Cary-100 spectrophotometer, before and after irradiation treatments.

According to obtained results, the continual light and UV-A and -B irradiation of BPheo*a* in methanol solutions results in its irreversible degradation. The corresponding absorption spectra were changed, showing continuous drop in absorbance of Q_y-band ($A_{Qy,max}$) during the treatments. BPheo*a* is significantly degraded by UV-A after 20 min and by UV-B after 10 min of irradiation. On the other hand, the results suggest that BPheo*a* shown significant stability against VIS light: it is little degraded after 30 min of treatment and after that period shown good stability - it is very difficult to degrade them even after 180 min. BPheo*a* degradation induced by VIS, UV-A and UV-B irradiation obeys first-order kinetics - results obtained from the kinetic analysis (from graphics $ln\ A_{Qy,max} = f\ (t_{irr})$) showed significant differences in the degradation rate constant values (k): the highest k-value is for UV-B irradiation treatment, $k = 0.04380\ min^{-1}$, then for UV-A irradiation, $k = 0.00520\ min^{-1}$, and for VIS treatment, $k = 0.00044\ min^{-1}$. Degradation of BPheo*a* induced by UV-B is fastest. The results are in accordance with the known fact that UV-B irradiation is more energetic in comparison with UV-A, and VIS at least: degradation is governed by photons energy input.

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Polymers and Polymer Materials (POL)

POL O-1

BIOMATERIALS FOR CONTROLLED THYMOL RELEASE PRODUCED USING SUPERCRITICAL CO_2

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Thymol is a natural compound present in thyme and oregano extracts. Due to its strong antimicrobial, anti-inflammatory and antioxidant activity, thymol is used for medical, food, agriculture, and veterinarian applications [1]. Entrapping of thymol into polymeric materials using supercritical impregnation process has been suggested for providing its controlled release [2]. Physical properties of supercritical carbon dioxide ($scCO_2$) such as low viscosity, high diffusivity and the absence of surface tension effects impart high penetrating capability of $scCO_2$ together with good mass and heat transport properties [3] and recommend $scCO_2$ for supercritical impregnation and foaming processes. Polymers especially attractive for researchers due to their biocompatibility, FDA approval and formability are cellulose acetate, poly(ε-caprolactone), and poly lactic-*co*-glycolic acid [2,4,5]. It was previously reported that cellulose acetate can be used as a pharmaceutical excipient and for controlled release of active substances [2], poly(ε-carpolactone) as a long term degradable implants with tailorable degradation kinetics [4], and poly lactic-*co*-glycolic acid as a porous platform for tissue engineering and drug delivery devices [6]. Therefore, present study was aimed to fabricate thymol containing porous carriers based on cellulose acetate, poly(ε-caprolactone), and poly lactic-*co*-glycolic acid using supercritical impregnation and/or foaming process. Supercritical impregnation process was optimized by variation of pressure, temperature and time. Morphology and release kinetics of the thymol containing carriers was studied. Obtained carriers had pores with diameter from 5 to 500 µm. Thymol release was tested in a phosphate buffer solution (pH 7.4) at 37 °C during one day to one month. Experimental data on release kinetics were correlated with Higuchi and Korsmeyer-Peppas release models. Results indicated that supercritical technology is promising process for green eco-friendly production of biocompatible systems for short (several hours) and long term (up to a month) delivery of thymol.

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POL O-2

POLYURETHANE/GRAPHENE OXIDE GRAFTS FOR TISSUE ENGINEERING

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Modern tissue engineering aims to create materials which promote, possibly in a controlled way, cell adhesion. They cannot be considered as a standing substitute of a tissue, but as a temporary structure which promotes regeneration. In this work, a biodegradable polyester urethane (Degrapol) was used as a matrix which mechanical, electrical and cell adhesion properties ought to be modified by addition of graphene oxide (GO). Using solution electrospinning method, samples containing different quantities of GO (0.5-2.0 wt%) were obtained [1]. In order to produce fibrous scaffolds with increased porosity, solutions of DP and GO were co-spun with a water soluble polymer, polyethylene oxide (PEO), which was subsequently removed. Morphological and mechanical properties of the scaffolds were analyzed, and it was found that the addition of GO had not changed much the morphology of the obtained fibrous net. The co-electrospining of the polymers was successfully performed resulting in a mesh formation consisted of both polymers. The tensile test showed that the presence of GO in the matrix increased the tensile strength up to 7.15 MPa. The obtained porous scaffolds were used to heal an artificial lesion of connective tissue. The experiment was performed on white laboratory rats Wistar strain according to the procedures for the use of experimental animals for scientific purposes. Histological tissue analysis was performed 3 months after the application of scaffolds. The results show degradation of the scaffolds, absence of an inflammatory process and penetration of tissue cells in the scaffolds. It can be concluded that the porous scaffolds are biocompatible, which may have practical application in the human and veterinary medicine.

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Keywords: tissue engineering; electrospinning; biodegradable polyurethane.

POL O-3

FLEXIBLE THERMOPLASTIC POLYURETHANE/ZnO NANOCOMPOSITE FOAMS FOR BIOMEDICAL APPLICATION

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Thermoplastic polyurethanes (TPUs) are widely used polymers in biomedical application due to their excellent biocompatibility [1]. A variety of properties in these materials could be obtained by controlling the structure of their soft and hard segments.

In the present study TPU obtained by polymerization from dimers of fatty acids [2] was used to produce TPU/ZnO nanocomposite foams by thermally induced phase separation method (TIPS). The content of nano filler was varied between 0.5 and 10 wt % related to the polymer.

The physicochemical characteristics of the prepared foams were observed by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). The physical properties were evaluated by measuring the absorbency, fluid handling capacity, contact angle measurements and water vapor permeability.

The presence of ZnO nanofiller additionally affects the mechanical and biological properties of TPU nanocomposites.

The results indicate that TPU/ZnO nanocomposite foams have considerable potential as wound dressing materials as well as material for tissue engineering of blood vessels.

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Keywords: nanofiller, foams.

POL O-4

OPTICAL, STRUCTURAL AND MECHANICAL PROPERTIES OF SOL-GEL ORGANIC – INORGANIC HYBRIDS, OBTAINED BY CO-CONDENSATION OF TWO UREASILICATE STOICHIOMETRIC PRECURSORS

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In this study two hybrid organic-inorganic ureasilicate monomers with different length of polymer segments were chosen for preparation of sol-gel material that includes two moieties blended on the molecular scale. The monomers were obtained by rapid uncatalyzed reaction between amino and isocyanate functional groups which make up parts of constituent of two modified silica ethoxides and a polyetheramine. In particular, O,O'-bis(2-aminopropyl)-polypropylene glycol)-block-polyethylene glycol-block-polypropylene glycol-500 (Jeffamine ED-600) and (triethoxysilyl)propyl isocyanate (ICPTES) were used for synthesis of the first monomer and (aminopropyl)triethoxysilane (APTES) and 3-(triethoxysilyl)propyl isocyanate (ICPTES) were used for synthesis of the second monomer respectively. One-pot sol-gel route was applied to transform the monomer blend to transparent xerogles. The prepared samples were characterized by optical UV - VIS spectroscopy, small-angle X-ray scattering (SAXS), FTIR spectroscopy and depth sensing indentation method (DSI). It was established, that tuning of the mechanical properties of the material was achieved by simple variation of volume ratio between the monomers. A morphological model for siloxane-polymeric ureasilicate with different concentration of monomers was proposed.

The results suggest that the obtained materials are potentially applicable for fabrication of photochromic devices, nonlinear optical elements, bioelectrodes and proton conducting polymer membranes for hydrogen fuel cells.

Keywords: ureasil, organic-inorganic, hybrid material, ureasilicate.

POL P-1

INVESTIGATION OF THE STRUCTURE AND SURFACE PROPERTIES OF NOVEL POLYURETHANE NETWORKS BASED ON POLYCAPROLACTONE

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Polyurethane networks (PUN) represent versatile materials which are usually consisted of different hard (HS) and soft segments (SS). They possess very good mechanical, thermal and surface properties. Such properties originate from their different composition, chemical structure of the crosslinking agent and molecular weights of the HS and SS [1].

In this work, series of PUNs was obtained by catalyzed two-step polymerization method in the solvents mixture. The PUNs were based on polycaprolactone macrodiol that represents SS and 4,4'-diphenylmethane diisocyanate and Boltorn® hyperbranched polyester of the second pseudo generation which were selected as the HS. Six PUNs were synthesized with different content of SS (from 10 to 60 wt.%).

The structure and surface properties (morphology, swelling behavior and water absorption) of the synthesized PUNs was examined in order to investigate these materials for potential application in coatings.

Acknowledgements: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project no. 172062 and III43009).

Keywords: polyurethane networks; polycaprolactone; hyperbranched polyester; surface properties; coatings.

POL P-2

SILVER(I) ADSORPTION ON MAGNETIC MACROPOROUS CHELATING POLYMER

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Environmental poisoning due to the emission of waste silver electrical and electronic industries, jewelry, photography and dentistry, in the last few decades has been of growing concern. The most effective methods for silver removal from aqueous media include electrolysis, precipitation, ion-exchange and adsorption. Highly crosslinked GMA-based polymers are chemically and mechanically stable materials containing reactive epoxy groups susceptible to undergoing functionalization, thus allowing the attachment of complexing agent selective for a specific metal ion.

In this presentation, macroporous chelating glycidyl methacrylate and ethylene glycol dimethacrylate copolymer functionalized with diethylene triamine (PGME-deta) was tested as Ag(I) sorbent from aqueous solutions. The sorption kinetics was studied in batch experimental mode and static conditions at room temperature and different initial Ag(I) concentration. The results were fitted to surface-reaction (pseudo-first and pseudo-second-order) and particle diffusion-based (intraparticle diffusion and Boyd's) kinetic models.

The pseudo-second-order model provided the best fit for the kinetic data, with a definite influence of pore diffusion. The maximum sorption capacity at pH 6 of 2.25 mmol g^{-1} (240 mg g^{-1}) was reached after 30 minutes. Equilibrium data were analyzed with Langmuir, Freundlich and Temkin adsorption isotherm models.

Keywords: Chelating polymer, silver(I) adsorption, kinetic models, adsorption isotherms.

POL P-3

ANTIMICROBIAL COMPOSITE POLYMERS AS POTENTIAL AGENTS IN CHRONIC WOUND HEALING

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Not presented.

POL P-4

HIGH PRESSURE FUNCTIONALIZATION OF BIO-COMPOSITE FILMS WITH THYMOL

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Active packaging is an innovative concept which implies a modification of a packaging material in order to enable prolonged shelf life or enhanced quality or sensory properties of food products [1]. Packaging material can contain antimicrobial and antioxidant substances, as well as indicators for monitoring food freshness, time-temperature indicators or seal and leak indicators [1]. Since it has been generally recognized as safe (GRAS) by the United States Food and Drug Administration (FDA), thymol, a natural substance with proven antimicrobial properties, was found to be a promising bioactive agent for active packaging purposes [2–4]. Conventional techniques such as solvent casting, melt blending or compression molding are commonly used for loading of thymol into polymers. Favorable properties of supercritical carbon dioxide (scCO_2) make the supercritical solvent impregnation (SSI) advantageous technique for incorporation of valuable substances into polymers compared to conventional methods [5,6]. SSI allows polymer processing at relatively low temperatures without utilization of organic solvents, while the homogeneous distribution of an active component throughout the whole polymer is accomplished [5,6]. SSI was used for functionalization of linear low-density polyethylene (LLDPE) [7], poly lactic acid (PLA) [8] and PLA with 5% of poly(ε-caprolactone) [9] with thymol.

In this study supercritical fluid technology was applied for functionalization of starch-chitosan films with thymol. Chitosan solutions (1% and 2%) and starch solution (1%) were used for fabrication of films with starch and chitosan mass ratios of 1/1 and 1/2. Films were impregnated with thymol in supercritical carbon dioxide at temperature of 35 °C, pressure of 30 MPa and impregnation time of 4, 7 and 18 h, using a static mode of operation. The results revealed that the highest loadings were achieved after 18 h of the impregnation process. The mass ratio of starch and chitosan in bio-composites influenced the SSI in the case of films synthesized from 1% chitosan solution. Namely, higher loadings of films with mass ratio 1/1 (up to 10.80%) were obtained, compared to films with 1/2 mass ratio (up to 6.48%). Thymol loadings of bio-composites fabricated from 2% chitosan solution were in the range of 0.83% to 3.25% for both starch chitosan mass ratios. FTIR spectroscopy confirmed the presence of thymol on the surface of the prepared films.

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POL P-5

ELECTROCHEMICAL SURFACE MODIFICATION OF GLASSY CARBON ELECTRODE BY 2D COVALENTLY BONDED THIN POLYMERIC FILM COMPOSED OF HETEROCYCLIC MOIETIES

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Surface modification of materials is accomplished using a vast number of molecules that possess a special affinity (SAMS) or are prone to undergo chemical reactions with the surface groups of the substrate- usually hydroxylated oxide layers (phosphonic or carboxylic acids, silanes, etc.). Probably the most direct mode to achieve this task is the use of the diazonium salts. This surface modification permits an easy way for tuning the properties of materials and adding some new interesting functionality that can be explored for: sensor construction, corrosion protection, catalysis, etc. In this work, we explored the use of diazonium heterocyclic compound to graft the surface of the glassy carbon electrode through direct grafting (by the isolation of the diazonium salt) and "in situ" electrochemical reaction of the transformed amino heterocyclic moiety into the corresponding diazonium salt. The grafted surface is analyzed by a number of electrochemical and surface analysis techniques.

Acknowledgements: Erasmus+.

Keywords: grafted surface, grafted surface, sensor, corrosion protection.

POL P-6

TRIBOLOGICAL BEHAVIOR OF POLYMER COMPOSITES INTENDED FOR PNEUMATIC VALVE SPOOL

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The friction behavior inside the pneumatic valve with NBR seals and spools made of new advanced polymer composite material has been previously studied within the EUREKA project [1]. The tribological characteristics were determined experimentally by measuring static and dynamic friction force as a function of spool velocity. The composite spools were manufactured by filament winding or laminating technology, followed by fine-tuned turning machine treatment in order to achieve certain complex valve geometry within the prescribe tolerances. Glass and carbon fibers/fabrics were used as reinforcements of epoxy and phenolic resins to produce composite material for the valve spool manufacturing.

It is known that the frictional forces in pneumatic valves are determined by many factors, such as material, shape and dimensions of both the spool and the seal, surface roughness, lubrication, temperature, etc. The obtained results have shown different dynamic friction force distribution for each of the spools made of PCMs, which was ascribed to different surface roughness and material's characteristics [2].

In this work we would like to point out some other aspects important for deeper understanding of the tribological behavior of polymer composite materials, that have not been discussed earlier [3].

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Keywords: polymer composites, tribology.

POL P-7

ELECTRICAL PROPERTIES AND CHARACTERIZATION OF POLYMER MATRIX COMPOSITES REINFORCED WITH GRAPHENE, MWCNTS AND A MIXTURE OF GRAPHENE, MWCNTS AND FULLERENES

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Not presented.

POL P-8

THE ROLE OF MODIFICATION PROCESS ON PROPERTIES OF REVERSE OSMOSIS MEMBRANES

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Not presented.

POL P-9

NANOSIZED POLYMER STRUCTURES FORMED FROM DIBLOCK COPOLYMERS BASED ON POLY(ALLYLGLYCIDYL ETHER) AND POLYGLYCIDOL IN WATER

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Polymer science, as an integral part of the chemical science, works towards ensuring the needs of society for new materials. Nanomaterials enter intensively in a number of areas, including biology and medicine. Their specific physico-chemical and mechanical properties are studied and particular attention is paid to the biocompatibility and biodegradability of the materials. A variety of copolymers with different architecture, topology and functionality of the chain, that exhibit huge potential for creation of supramolecular nanoparticles with preliminary defined properties, are obtained through controlled polymerization techniques. Polymer nanoparticles, obtained by self-association and/or co-association, find important applications as carriers of drugs, genes, diagnostic and therapeutic agents.

This work aims at studying the behavior of novel diblock copolymers based on poly(allylglycidyl ether) and polyglycidol in aqueous solution. The copolymers contain a hydrophobic residue and are obtained by ring-opening anionic polymerization. They are spontaneously soluble in water and form stable dispersions in appropriate concentration ranges. Full characterization of the resulting aggregates through dynamic and static light dispersion is performed. The critical aggregation concentrations as well as particle size distribution, hydrodynamic dimensions, molar masses, radii of gyration, and second virial coefficients of the nanoparticles are determined. The copolymers and their aggregates are promising carriers of biologically active substances and are suitable platforms for further chemical modification.

Keywords: polyglycidol, poly(allyl glycidyl ether), diblock copolymers, aqueous solution properties, light scattering.

POL P-10

DIELECTRIC PROPERTIES OF EPOXY/GRAPHITE FLAKES COMPOSITES

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Electrically conductive nanocomposites based on polymers, embedded with various kinds of graphite particles; exfoliated graphite, natural graphite, graphene flakes, etc. have been investigated as a promising material for electromagnetic interference shielding, thermoelectric applications and production of solar panels. For this work, various composite materials based on bisphenol-Aepoxy resin filled with exfoliated expanded graphite (EEG) or graphite flakes (GF), were prepared. Their dielectric properties were investigated in wide temperature (170-370 K) and frequency (20Hz- 200 kHz) ranges. Exfoliated expanded graphite (EEG) flakes were obtained after prolong sonication of expanded graphite in alcohol (for 10 hours). Graphite flakes (GFs) were prepared by a mechanical milling of very pure graphite powder in a planetary mill with dominant shear component of the applied stress. Milling lasted for 20 hours in the presence of water as lubricant, without (GF0) or with addition of surfactant: Triton-100x (GF-Tr100x) or KOH (GF-KOH).The influence of graphite flake thickness, shape, and surface chemistry on the dielectric properties of composites, for the load content of 5 wt% have been studied.

Acknowledgements: Authors are grateful to the Ministry of Education, Science and Technological Development of the Government of the Republic of Serbia for funding the study under the Projects (OI 171029).

Keywords: graphene flakes; polymer matrix composites; dielectric properties.

POL P-11

THE INFLUENCE OF GRAPHITE LOAD CONTENT ON DIELECTRIC PROPERTIES OF COMPOSITES

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For this work, composites based on bisphenol-A epoxy resin embedded with graphite flakes (GFs), of different load content of 6, 10 and 15 wt% GFs, were prepared. The frequency and temperature dependences of dielectric properties of such obtained composites were investigated in wide temperature (170-370 K) and frequency (20Hz - 8 MHz) ranges. The influence of the graphite load content on the dielectric permittivity (e_r), dielectric loss (tan*d*) and *ac* conductivity of composites, have been analyzed. Epoxy-based composite with a graphite content of 15 wt% shows significant changes in the temperature dependence of dielectric losses and *ac* conductivity at all frequencies, in comparison with the composites with the load content of 10 wt% and 6 wt%.

Acknowledgements: Authors are grateful to the Ministry of Education, Science and Technological Development of the Government of the Republic of Serbia for funding the study under the Projects (OI 171029).

Keywords: dielectric response, ac conductivity, nanocomposites.

POL P-12

SYNTHESIS OF REDUCED GRAPHENE OXIDE/MULTIWALLED CARBON NANOTUBES/POLYMER NANOCOMPOSITES

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The synthesis of polymer nanocomposite reinforced with reduced graphene oxide/multiwalled carbon-nanotubes (rGO/MWCNT) hybrid was performed via water-borne synthesis technique using two different approaches: in-situ synthesis by semi-batch emulsion polymerization and ex-situ synthesis by emulsion mixing. Water-borne synthesis of polymers is preferred method due the large number of advantages that they possess over the methods that involve organic solvents. Also is reported that with the in-situ synthesis the nanocomposites exhibit better properties due the formation of stable interactions between the reinforcement and the matrix, which is not case with the ex-situ synthesis [1].

The monomer system was containing methyl methacrylate (MMA), butyl acrylate (BA) and glycidyl methacrylate (GMA) in the following weight ratios 49.5/49.5/1, respectively. The rGO/MWCNT hybrid was prepared by ultrasonication of graphene oxide and MWCNT in two different weight ratios 1/10 and 10/1, followed by reduction with ascorbic acid. According to Tang and al. is expected that MWCNT will act as a bridges that connect the rGO sheets and on that way with lower percentage of hybrid will appear higher improvement of the nanocomposite properties [2]. The nanocomposite films were obtained by water evaporation.

The rGO/MWCNT hybrids were examined by transmission electron microscopy (TEM) in order to examine the distribution of the MWCNT and the rGO sheet, and Raman spectroscopy was employed for investigation of the chemical composition and structure of the hybrids.

For examination of the morphology of the nanocomposites was employed a scanning electron microscopy (SEM), the mechanical properties of the films were determined by tensile test measurement and dynamical mechanical analysis (DMA) was used for studying the viscoelastic properties of the nanocomposites.

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Keywords: polymer nanocomposites, reduced graphene oxide/multiwalled carbon-nanotubes, Raman spectroscopy, TEM, SEM and DMA analysis.

POL P-13

PULSED LASER DEPOSITON AND CHARACTERISATION OF PLATINUM- AND PALLADIUM-DOPED GRAPHENE THIN FILMS

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As a class of functional materials, noble metal nanoparticles display unique physical and chemical properties. Recently, these nanostructures have been used in combination with carbonaceous materials, such as graphene [1]. The graphene-noble metal composites find applications in a number of areas, including surface-enhanced Raman scattering (SERS), catalysis, and electrochemical sensing [2]. In this work, we employ the pulsed laser deposition (PLD) technique to fabricate noble metal-doped graphene films with potential use as gas sensors.

The PLD process for graphene was conducted under vacuum, whereas the ablation of the platinum (Pt) and palladium (Pd) noble metal targets was performed in presence of argon (ranging from 2 to 10 Pa). Results from scanning electron microscopy of the film surface show a mostly uniform and compact layer of graphene nanoplatelets. Successful deposition of Pt and Pd is confirmed by evaluating the elementary composition of the deposits using energy-dispersive X-ray spectroscopy. The use of higher pressures of argon as background gas decreased the absorbance of the films, as determined by ultraviolet and visible (UV/Vis) spectroscopy. Water contact angle measurements reveal that decorating the surface of graphene with metal nanoparticles increases its hydrophobicity. It is considered that the obtained graphene-based films are good candidates for use in gas sensing applications.

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Keywords: pulsed laser deposition, graphene, platinum, palladium, thin film.

POL P-14

SYNTHESIS OF GRAPHENE NANORIBBONS/POLYMER NANOCOMPOSITES AND ITS REINFORCING EFFECT

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The extraordinary mechanical properties of graphene nanoribbons allow its incorporation into a wide range of polymeric nanocomposites materials. The quasi one-dimensional nature of GNRs results in additional advantages over graphene sheets, especially the high aspect ratio of GNRs may significantly decrease the mechanical percolation threshold in the polymer composites.

The aim of this research work was to investigate the mechanical properties of water–borne graphene nanoribbons (GNRs)/polymer nanocomposites synthetized via emulsion mixing technique. The polymer system is composed from p(MMA/BA/acrylamide), in ratio 49.5/49.5/1wt%, with 50 % solid content, obtained by semi-batch emulsion polymerization. The polymer was reinforced using GNRs water dispersion in presence of polyvinyl pyrrolidone (PVP) by means of sonication. Indeed the stable GNRs dispersions were mixed in different ratios in order to prepare 0.2 wt%, 0.4wt%; 0.6 wt%; 0.8 wt% and 1wt% of GNRs in relation to polymer. The composite films were formed by water evaporation under controlled temperature and humidity conditions and further characterized by means of tensile test measurement and DMTA for studying the mechanical, thermal and viscoelastic properties of the nanocomposites.

The composite blends are distinguished with improved mechanical and thermal properties compared to the neat polymer and this effect increased with higher loading of GNRs. This is likely due to improved interaction between the polymer chains and the GNRs that offer an important interface on the edges, reach in oxygen functional groups. The presence of these edges facilitates the interactions with polymer chains, resulting in important reinforcing effect.

Keywords: graphene nanoribbons, polymeric nanocomposites materials, mechanical, thermal and viscoelastic properties.

POL P-15

DIELECTRIC PROPERTIES OF BIOCOMPOSITES OF POLYPROPYLENE WITH OATS AND RYE BRAN

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In the past few decades, companies and scientists are driven to find alternative materials for conventional non-renewable and limited fossil fuel resources. Biocomposites, which consist of biomass and polymers, have proved to be a good alternative both from the economic and environmental point of view. The most important advantages of natural fillers such as lignocellulosic biomass are their non-toxicity, availability, renewability, biodegradability, low density per unit volume, and low cost. Biocomposite materials have a wide range of uses for consumer goods, as well as for automotive, transportation, construction, and packaging applications.

The focus of this work was design and investigation of dielectric properties biocomposites of isotactic polypropylene with the different percent of oats and rye bran. Isotactic polypropylene was blended with various proportions of oats and rye bran (20%, 30%, and 40%), using Brabender plastograph operating at 170 °C. Pure isotactic polypropylene and isotactic polypropylene/bran samples were then removed from the plastograph as small clumps and molded at 175 °C in a hydraulic hot press.

Measurements of dielectric properties were performed at 13 frequencies in the range from 30 Hz to 30 kHz at room temperature of 25 °C. Values of effective dielectric permeability and dielectric loss tangent remain nearly constant over the whole frequency range for a sample of pure isotactic polypropylene, while for biocomposites they decrease with the increase of frequency. The obtained results showed that incorporation of oats and rye bran into polymer matrix increases values of dielectric properties in the entire frequency range. When the weight percentage of bran was increased in polymer matrix dielectric properties were found to increase.

Acknowledgements: Authors are grateful to the Ministry of Education, Science and Technological Development of the Government of the Republic of Serbia for funding the study under the Projects (OI 171029).

Keywords: biocomposites, effective dielectric permeability, dielectric loss tangent.

POL P-16

ORGANICALLY MODIFIED SILICATE HYBRIDE MATERIALS AS SENSING LAYERS FOR ENZYME IMMOBILIZATION IN AMPEROMETRIC BIOSENSORS

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Organic-inorganic ureasilicate nanocomposites were synthesized and investigated in order to be used as a potential enzyme immobilization material in an electrochemical biosensor for detection of organic pollution in water. The aim of the present work is to study the sensitivity of a biosensor with bioenzyme laccase, immobilized with chalcogenide-containing ureasilcate material. 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) was chosen as a substrate for determination of laccase activity. In order to evaluate the efficiency of immobilization of laccase with the chalcogenide composite, a comparison of the sensor characteristics with a similar bioelectrode in which the enzyme was immobilized with a pure ureasilicate was performed.

Ureasilicate materials were prepared by hydrolysis and condensation of ureasilacate monomer, obtained by the reaction between organically modified silica ethoxyde (ICPTES) and polyetheramine (Jeffamine). As_2S_3-containing ureasilicate nanocomposites were synthesized by mixing the preliminary obtained ureasilicate monomer with As_2S_3 nanoparticles, dispersed in the organic solvent. Laccase enzyme was immobilized on the surface of the gold planar electrodes using the As_2S_3-ureasil composite as a matrix agent.

The biosensor's characteristics have been tested using cyclic voltamperometry and chronoamperometric measurements on the increasing concentration of ABTS. It was found that the biosensor based on the ureasil-chalcogenide glass composite is characterized by very high sensitivity (67540 $A.M^{-1}.m^{-2}$), 38 times higher in compare with pure ureasil (sensitivity of bioelectrode was calculated as 1762 $A.M^{-1}.m^{-2}$).

Keywords: organic-inorganic ureasil, laccase, amperometric biosensor.

POL P-17

EPOXY-SILICONE HYBRIDS FOR COATINGS APPLICATION

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Epoxy-silicone hybrids are relatively new systems intended for improving the use of epoxy resins in protective coatings technology.

The aim of this comparative study is to analyze cross-linking of epoxy-silicone hybrid hardened systems, formed by two different approaches: cross-linking of well-defined building blocks (hydrogenated DGEBA with amino-functional silicon resin) in opposite to simultaneous forming of organic and inorganic phase (cross-linking using hybrid epoxy-silicone resin with aminosilanes). The influence rising from these two approaches on the overall properties of cross-linked systems was analyzed in this study.

The reactive components and hardened systems were analyzed by thermogravimetric analysis up to 600°C. Characteristic bands and glass transition temperature of the cured systems were determined using FT-IR spectroscopy and DSC measurements respectively. The chemical resistance of the obtained 200 microns films, free from external restrain, was performed using method for determination of the effects of immersion in liquid chemicals [1]. Swelling resistance was observed in several groups of testing liquids where each of them is representing whole class similar acting substances [2]. Evaluation of mechanical properties was performed using techniques for determination of indentation hardness, rapid deformation (impact resistance), abrasion resistance and adhesion to metal substrate of cross-linked systems.

Different amount of SiO_2 residues were determined depending on the analyzed system. It was shown that 34% of SiO_2 residue compared to 10% which is originating from the siloxane domain of epoxy-silicone hybrid molecule could be built up during cross-linking process using aminosilanes agents [3]. In contrast, cross-linked system which is made using amino-functional silicone resin, gives 23% wt. of SiO_2 residue.

Glass transition temperature of cured samples with values over 50 °C and the good mechanical properties are indicating convenience of the cross-linked systems.

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Keywords: epoxy-silicone hybrid resin; amino-functional silicone resin; chemical resistance; resistance to indentation; impact resistance; abrasion resistance; adhesion.

POL P-18

COMPARISON OF GLASS TRANSITION TEMPERATURE VALUES OF CYANATE ESTER RESIN OBTAINED BY TMA, DMA AND DSC METHODS

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For analysis of the temperature-dependent properties of the resin systems, thermal analysis instruments are used. These instruments give a lot of useful information regarding the resin systems, which are necessary in the field of advanced composites for determination of their area of application. The glass transition temperature is one of the most important property for a resin system, because it gives information for the temperature limitation on which that particular resin system can be used.

In this research, the glass transition temperature of cyanate ester resin is determined by using three thermal analysis methods: thermomechanical, dynamic-mechanical and differential scanning calorimetry method. The three Tg values obtained by each of these three methods are compared. The thermal analysis instruments used in this research are from the Netzsch brand, Germany.

The results confirmed that the Tg values differ by 10-20^0 C in the three methods for thermal analysis.

Keywords: thermal analysis, cyanate ester resin, glass transition temperature.

POL P-19

THERMAL ANALYSIS OF EPOXY RESIN SYSTEM

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By thermal analysis, a lot of useful information can be determined regarding resin systems. The information obtained from the thermal instruments have great significance in the technology of advanced composites. By using them, it can be determined the degradation temperature, the glass transition temperature, the activation energy, as well as the course of the polymerization process.

In this research, the mass loss temperature of the epoxy resin is determined by TGA analysis, and by using several different heating rates the degradation energy is also determined. By DMA analysis is determined the glass transition temperature and Ea. The DSC method is used for determining the polymerization kinetics of the epoxy resin. The thermal instruments used in this research are from the Netzsch brand, Germany.

From the TGA analysis, the decomposition and loss of mass in this resin is at a temperature of approximately 300 °C. The Tg value through DMA for the epoxy resin is 214 °C, and the Tg value through DSC is 200^0C. Ea from DMA is 735.24 kJ/mol.

Keywords: epoxy resin, thermal analysis, glass transition, activation energy, degradation, polymerization.

POL P-20

SYNTHESIS AND CHARACTERIZATION OF NEW PEG – BACTERIAL CELLULOSE NETWORKS

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Not presented.

POL P-21

ISOTHERMAL CRYSTALLIZATION OF ISOTACTIC POLYPROPYLENE NUCLEATED WITH PIMELATES OF EARTH-ALKALINE ELEMENTS

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Ba, Sr, Ca and Mg pimelates were used as nucleators for the crystallization of isotactic polypropylene. The pimelates were synthesized as described earlier [1] and they were obtained as white powders. Their average grain size and distribution were determined, and for Ca- and Ba-pimelates the grain size was less than 10 microns, while larger dimensions were found for Mg- and Sr-pimelates (29 and 22 microns). Isothermal crystallization of polypropylene was analyzed by DSC. The crystallization was carried out at the T_c in the range from 397K to 406 K. Based on the determined values for the enthalpy of crystallization, the extent of crystallization (crystal conversion) was calculated and the half-time of crystallization ($t_{0.5}$) was determined and used as a parameter to compare the rate of crystallization in differently nucleated systems. It was shown that the value of $t_{0.5}$ for Ca-pimelate nucleated polyprolylene was lower than for all other nucleated systems. The content of the β-crystalline phase in polypropylene nucleated with different pimelates has a decreasing tendency with the increasing of crystallization temperature, T_c. The equilibrium melting temperature for the nucleated polypropylene was in the range T^0_m=446-455 K, lower than for non-nucleated isotactic polypropylene (460 K).

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Keywords: polypropylene, pimelates, polypropylene.

Chemical Engineering (CE)

CE O-1

OPTIMIZATION OF BIODIESEL PRODUCTION FROM MUSTARD OIL

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CE O-2

A NOVEL PROCESS OF HYDROCARBON GROUPS OF GAS OIL FRACTIONS

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Not presented.

CE P-1

TRANSESTERIFICATION OF LOW GRADE EDIBLE OIL MIXTURES: MUSTARD OIL, RAPESEED OIL AND PEANUT OIL

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Not presented.

CE P-2

HYDRODYNAMIC CHARACTERISTICS OF SPRAY LIQUID-LIQUID EXTRACTION COLUMN

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Hydrodynamics of a pilot plate spray liquid-liquid extraction column ($D = 10.0$ cm; $H = 273.5$ cm) was investigated. The experimental data of the hydrodynamic characteristics, such as slip velocity (U_s), dispersed-phase holdup (ε_d), Sauter mean diameter (D_{32}) of droplets, as well as axial dispersion coefficient (E_c) were obtained using two-phase toluene-water system, with toluene as dispersed and water as continuous phases. On the basis of experimental data obtained in the present paper, the relationship between dispersed-phase holdup and phase flows was presented. It was concluded that the dispersed-phase velocity (U_d) had a great impact on toluene holdup. Also, a strong effect of the continuous-phase velocity (U_c) on toluene holdup was evident. The effect of the dispersed-phase and characteristic velocities ratio (U_d/U_0) on the dispersed-phase holdup was shown. It was observed that the dispersed-phase holdup tends to increase when the dispersed-phase and characteristic velocities ratio was increased. The effects of phase velocities (U_d, U_c) and toluene holdup on Sauter mean diameter of droplets and axial dispersion coefficient were studied. The results applied in the present paper show that the values of D_{32} decreased with an increase of the dispersed-phase velocity, when the continuous-phase velocity remained constant. On the other side, no correlation between D_{32} and the continuous-phase velocity was found. Based on the experimental data, obtained in the present paper, it was revealed that axial dispersion coefficient decreased linearly with an increase in the continuous-phase velocity when the dispersed-phase velocity was constant. On the other hand, it was found that E_c was independent of the dispersed-phase velocity in the range of the U_d of 0.445 to 0.637 cm/s.

Acknowledgements: Ministry of Science and Technology.

Keywords: spray extraction column; slip velocity; Sauter mean drop diameter; axial dispersion coefficient.

CE P-3

PRODUCTION OF PYROLYTIC LIQUID FUEL OVER SiO_2 CATALYST

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The continuous rising of waste plastic disposal is undesirable due to environmental concerns, rising costs, and poor biodegradability. Catalytic pyrolysis over natural catalysts is environmentally and economically acceptable method for conversion of waste.

In the present investigation, a waste mixture of high-density polyethylene and polypropylene was chosen as a raw material. All experiments were carried out in a laboratory semi-batch reactor using quartz sand (SiO_2) as a natural catalyst. The objective of catalytic pyrolysis is the optimization of the working parameters at a temperature range of 400 °C to 550 °C and dynamic conditions, in order to produce a high yield of liquid fuel. The obtained results showed that the yield of liquid fuel was dependent on the time of pyrolysis, as well as the amount of raw material. The physical properties (density, kinematic viscosity, and refractive index) of the obtained pyrolytic oil were close to those of mixture of petroleum products.

Keywords: catalytic pyrolysis, waste plastic, quartz sand, physical properties.

CE P-4

CHEMICAL COMPOSITION OF LIQUID FUEL OBTAINED BY WASTE PLASTIC PYROLYSIS OVER NATURAL CATALYST

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Catalytic thermal degradation is a useful method for the conversion of the plastic waste into valuable chemicals and oil products.

The focus of this work is characterization of liquid oil product obtained from catalytic pyrolysis of waste polyolefin mixture under dynamic conditions. Catalytic pyrolysis of waste HDPE/PP pellets was done in a semi-batch reactor at a temperature range of 400 °C to 550 °C and at a heating rate of 10 °C min^{-1}. Liquid product identification and quantification was done using different analytical techniques. A gas chromatography with mass spectrometry (GC/MS) and infrared spectroscopy (FT-IR) were used for chemical characterization. It was found that the derived liquid products were hydrocarbons, mainly consist of alkanes and alkenes and their isomers with wide carbon number distributions. The detailed analysis of various characteristic functional groups present in the oil was done using FT-IR.

Keywords: catalytic pyrolysis, waste HDPE/PP mixture, quartz sand, GC-MS, FTIR.

CE P-5

OPTIMIZATION OF DESULFURIZATION AND DEAROMATIZATION OF GAS OIL FRACTIONS

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Not presented.

CE P-6

1,3- AND 1,4-DIIODOTETRAFLUOROBENZENE AS HALOGEN BOND DONORS IN CRYSTAL ENGINEERING

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Halogen bond (XB) is an attractive, strong and directional noncovalent interaction between chemical entity with usually covalently bonded and partially positively charged halogen atom (halogen bond donor) and some Lewis base.[1] This interaction has attracted considerable attention in the solid state chemistry, where it is widely used for the synthesis of the new materials. The most usual halogen bond donors in solid state chemistry are perhalogenated hydrocarbons, of which 1,4-diiodotetrafluorobenzene (**1,4-tfib**) is probably the most extensively used halogen bond donor to date, while 1,3-diiodotetrafluorobenzene (**1,3-tfib**) has remained almost completely unexplored (18 crystal structures in CSD).[2] This study investigates the structures of 14 new cocrystals of the bent 1,3-diiodotetrafluorobenzene and 9 new, analogous cocrystals of linear 1,4-diiodotetrafluorobenzene, with 9 monotopic and 7 ditopic nitrogen-based aliphatic and aromatic halogen bond acceptors. In particular, whereas our comparative study of **1,3-tfib** and **1,4-tfib** cocrystals with used halogen bond acceptors reveals a similarity in I···N halogen bond lengths and distribution of melting points of explored cocrystals, it also reveals differences in stoichiometric compositions of cocrystals and the structures of underlying halogen-bonded motifs. Tentatively, the herein observed differences in halogen-bonded motifs and cocrystal composition are explained through changes in the efficiency of crystal packing upon switching from a linear halogen bond donor to the bent **1,3-tfib**. This implies that, at least in some cases, close packing, rather than halogen bonding strength may be the force that determines the supramolecular architecture and stoichiometric composition of the final the product.

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Keywords: crystal engineering; halogen bond; cocrystals.

CE P-7

APPLICATION OF VENTILATION VENTS IN POLLUTED ENVIRONMENT

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The present study was conducted in order to evaluate efficiency of a personal body cooling systems based on ventilation technologies and its effects on test subject's physiological suitability during exertional heat stress in hot environment and usage of impermeable CBRN protective suit. Performed results are based on realized tests in especially unique designed testing ground. Six male test subjects were subjected to exertional heat stress test consisted of two cycles of specific working activities in hot environment. As a physiological strain indicator the following parameters have been determined: mean skin temperature, auditive temperature, heart rate and sweat rate. Results confirmed that cooling vest worn under the impermeable protective clothes was able to attenuate the physiological strain levels during exercise, when compared to identical exposure without the cooling system.

Keywords: impermeable protective clothing, heat stress, cooling vest, strain indicators.

CE P-8

THE INFLUENCE OF EXTRACTION TECHNIQUE AND THE TYPE OF SOLVENT ON THE ANTIOXIDANT ACTIVITY OF THE BLACK MUSTARD OIL (*Brassica nigra*)

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Black mustard (*Brassica nigra*) is a weed that grows mainly in fields and landfills while its seed oil exhibits antioxidant properties during *in vivo* testing [1]. The present paper deals with the antioxidant activity of the black mustard seed oil (BMSO) provided by cold pressing, extracting with different solvents (*n*-hexane, trichlorethylene and with mixture of trichlorethylene and triethanolamine:glycerol (TEOA:G) deep eutectic solvents, molar ratio 1:2) and extracting with trichlorethylene after the pretreatment with TEOA:G. The percentage of antioxidant activity of oil was assessed by the DPPH (2,2-diphenyl-1-picrylhydrazyl) free radical assay. The antioxidant activity of BMSO is expressed as IC50 (concentration of oil necessary to neutralize 50% of the initial DPPH radicals` concentration). The best antioxidant activity is reported with BMSO obtained by extraction with trichlorethylene (IC_{50}= 5.673 mg/cm^3), followed by BMSO extracted with trichlorethylene after the pretreatment with TEOA:G (IC_{50}= 8.298 mg/cm^3), a mixture of trichlorethylene and TEOA:G (IC_{50}= 8.695 mg/cm^3) and cold pressing (IC_{50}= 9.147 mg/cm^3). BMSO extracted with *n*-hexane (IC_{50}= 13.909 mg/cm^3) showed significantly less antioxidant activity due to the degenerative effect of *n*-hexane on the antioxidants. On the bases of these results, BMSO can be classified as an oil rich in antioxidant components, and its antioxidant activity is affected by the extraction technique and the used solvent.

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Keywords: antioxidants, extraction, deep eutectic solvents, black mustard seed.

Textile Engineering (TE)

TE O-1

THE INFLUENCE OF 1,2,3,4-BUTANETETRACARBOXYLIC ACID ON IN SITU SYNTHESIS OF Cu-BASED NANOPARTICLES ON THE VISCOSE RAYON FABRIC AND ITS ANTIBACTERIAL ACTIVTY

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Ag nanoparticles are widely exploited as an efficient antimicrobial agent against various microorganisms [1]. However, recently Cu-based nanoparticles (NPs) increasingly gained much scientific attention due to relative inexpensive precursors and excellent antimicrobial activity against numerous bacteria strains. The development of antimicrobial textile nanocomposites comprising of Cu-based NPs (Cu, Cu_2O and CuO or their mixtures) became the focus of many research groups [2-4]. The dominant method for synthesis of Cu-based NPs relies on the introduction of carboxyl groups to cellulose fibers (cotton, viscose rayon...) by coating them with adequate polymer or chemical modification of cellulose, adsorption of Cu^{2+}-ions and their reduction with appropriate reduction agent. Hence, this study discusses the possibility of *in situ* synthesis of Cu-based NPs on viscose rayon fabric previously modified with 1,2,3,4-butanetetracarboxylic acid (BTCA) of different concentrations with an aim to obtain antibacterial protection. The changes in chemical structure of the viscose fibres were assessed by FTIR spectroscopy. The presence of NPs on the fabric was confirmed by FESEM, EDX and AAS analyses. Developed nanocomposite provided excellent antibacterial protection against Gram-negative bacteria *E. coli* and Gram-positive bacteria *S. aureus.* A release of Cu^{2+}-ions from nanocomposite in physiological saline solution was also investigated.

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Keywords: viscose, Cu nanoparticles, antibacterial protection.

TE O-2

THE INFLUENCE OF THE BLEACHING AND DYEING PROCESSES ON THE COMFORT PROPERTIES OF KNITTED FABRICS CONTAINING ELASTANE

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Comfort properties of knitted fabrics depend on various fabric characteristics such as chemical composition, knitted structure (fabric thickness and weight), air permeability and water vapour resistance. The purpose of this investigation is to study the influence of different elastane content and different processing stages (bleaching and dyeing) on the comfort properties of single jersey knitted fabrics. Samples made of 100% cotton (20 tex ring spun yarn) and elastane yarn (22 dtex multifilament yarn) in alternating courses (half plating) and elastane yarn in every course (full plating) were scoured, bleached or dyed. Bleaching was done with 50% H_2O_2 and dyeing in dark blue shade with reactive dyes.

In comparison with 100% cotton knitted fabrics, cotton/elastane fabrics have increase fabric thickness for about 5-16%, fabric weight for about 8-21%, and water vapour resistance for about 11-30%, but decrease air permeability for about 28-51%. Increased fabric thickness is a result of plating which means the simultaneous formation of one loop from two threads, so that one thread will lie on the face of the fabric, while the other thread is fed to the needles in such a way that it forms the back or reverse of the final fabric. In this case, the largest distance between two points of the cross section of the knitted fabric will increase because over cotton yarn is elastane yarn. With the increase of the fabric thickness, fabric weight increases too. 100% cotton knitted fabrics, being smoother and coarser as compared to cotton/elastane assist easier passage of water vapour and air through it, resulting in lower water vapour resistance and higher air permeability. The increased water vapour resistance and reduced fabric air permeability can be attributed to the higher thickness, fabric weight and compactness accompanied with a higher elastane content, which hard segments offer limited water vapour and air flow through knitted fabrics.

Insignificant differences in comfort properties (excluded air permeability) were found after different finishing stages. Bleached knitted fabrics have about 4-10% lower thickness, 4-11% lower fabric weight, 2-8% lower water vapour resistance, and 8-30% higher air permeability compared to dyed knitted fabrics. There are many factors that affect comfort properties, such us concentration of chemical agents, pH, temperature and duration of the treatment. Scouring and bleaching were done in high alkaline conditions with strong oxidative agent. In such conditions the cotton became stiffer, wax components were saponified, the fibers in yarns became closer, which resulted in a lower yarn cross-section and reduction of the fabric thickness, fabric weight and water vapour resistance. As the loop is clearer, the air permeability of bleached knitted fabrics is higher. On the other hand, dyeing in dark shade was done in milder conditions, which resulted in higher fabric thickness, fabric weight and water vapour resistance, and lower air permeability in regard to bleached knitted fabrics.

Acknowledgements: Authors are grateful to the Ministry of Education, Science and Technological Development of the Government of the Republic of Serbia for funding the study under the Project (OI 172029).

Keywords: cotton, elastane, knitted fabrics, comfort properties, bleached, dyed.

TE O-3

THE INFLUENCE OF ALKALI TREATMENT ON THE CHEMICAL COMPOSITION, SORPTION AND ELECTROKINETIC PROPERTIES OF JUTE WOVEN FABRICS

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In this investigation, the influence of alkali treatment on the chemical composition (content of hemicelluloses), sorption properties and surface charge of jute woven fabrics were studied. In order to partially remove hemicelluloses, jute fabric was alkali modified with NaOH solutions of different concentrations (5%, 10% and 17.5%) during 5 min at room temperature. With increasing the NaOH concentration, the content of hemicelluloses decreased. Untreated jute fabric has 21.76% hemicelluloses, while after alkali treatments, the content of hemicelluloses decreased down to 13.76%.The content of hemicelluloses has impact on various sorption properties, which can be evaluated by determination of moisture sorption and water retention value. Moisture sorption values provide information on the extent of areas accessible to water vapor within the fiber, while water retention value represented the total water holding capacity of fibers (i.e. all water absorbing and holding surfaces, cracks and cavities in jute fibers structures). Higher availability of hydroxyl groups which occurs as a result of removal of hemicelluloses, contributes to higher moisture sorption of alkali treated jute woven fabrics in relation to untreated. The moisture sorption of alkali treated jute fabrics increased for 17.3-21.6% in comparison with untreated fabric. Removal of hemicelluloses causes increase in water retention values. This is a consequence of structure changes (changes in the size and number of pores and microcracks in fibers) and effective removal of hydrophobic layer on the fabric surface (fats and waxes), which should enable better hydrophilicity. Alkali treatments during only 5 min can improve the water retention value up to 49%.

The changes of the fabric surface chemistry caused by removal of hemicelluloses also have influence on the electrokinetic properties, i.e. surface charge. Zeta potential measurements in a wide pH range were used for studying the surface charge of textile fabrics, including presence, availability and nature of surface groups. Untreated jute woven fabric has negative zeta potential in a wide range of pH due to the presence of hydroxyl and carboxyl groups on the surface subjected to dissociation in a high pH range. The greater accessibility of dissociated surface functional groups increases the ζ-potential. Alkali treated jute fabrics display a positive $\zeta_{plateau}$-value (zeta potential value in a basic range of pH) as a result of removal of fats, waxes and pectin from the fibers surfaces. Also, the effectiveness of such an alkali treatment process in order to increase the accessibility of surface groups can clearly be seen from the drastic change of the ζ-potential at low pH values as compared to untreated fabric. With increasing the concentration of NaOH from 5 to 17.5%, ζ-potential values decreased. Furthermore, isoelectric point (IEP, a pH value were ζ value is 0) as an indicator of the nature of functional groups of alkali treated jute fabrics are shifted toward higher pH. This indicates that after alkali treatment, contribution of acidic groups on the fiber surface become lower.

Acknowledgements: Authors are grateful to the Ministry of Education, Science and Technological Development of the Government of the Republic of Serbia for funding the study under the Project (OI 172029).

Keywords: jute, NaOH, hemicelluloses, sorption properties, zeta potential.

TE P-1

IMAGE ANALYSIS OF KNITTED FABRIC ROUGHNESS

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Texture is an important physical attribute of textiles, responsible for their appearance, handle, and functionality. Fabric texture varies between smooth and rough, quantified through the vertical deviation of its surface. Fabric roughness, or its opposite smoothness, can be employed as measure of the surface texture of fabrics. In general, texture depends upon the constructional parameters of the fabric, such as fibre properties, yarn count, yarn twist, fabric structure and fabric design.

Image analysis is an objective method used to define the surface properties of fabrics. The key application of image analysis is in quality control, for identifying fabric failures. Additionally, it can be used to identify fabric structure, along with finding application in different research, e.g. unevenness. Similarly, image analysis is appropriate for researching roughness as a fabric surface parameter.

In previous studies the authors have shown that simple scanned images of fabrics can accurately represent woven fabric roughness [1]. This research investigates mesoscopic scale images of knitted fabrics to extract the roughness information via 3D spectrograms. A set of samples in single jersey knit made of polyamide filaments, with linear density ranging between 17 dtex and 78 dtex, was used. The samples' images were obtained by using an OLYMPUS BX51 microscope with 5x zoom. The image analysis was conducted using the software package *R*. To standardize the analysis the original images were converted to grayscale. Subsequently, a histogram of grey frequencies from 0 (black) to 255 (white) was obtained. Darker colours in the histogram correspond to lower points in the fabric's topography. 3D spectrograms were then created, providing a visual representation of the fabric surface by transforming the grayscale frequencies in a spectrum ranging from dark blue to dark red. Image data were further grouped by mixing gray tones on the original image using blur filter until the standard deviation of histograms was reduced to 6. Finally, the blurred image was transformed in a 3D spectrogram by the same procedure as the original image.

Thresholds were set to describe the roughness/smoothness of fabrics. The first threshold defines the macro porosity between the loops of the knitted structure. Fabrics knitted from fine filaments (17 dtex) have larger pores which leads to a rougher surface. With the increase of the filament linear density the porosity decreases and a smoother fabric surface is obtained. The second threshold is used to characterize the topography amplitudes on the fabric's surface. Fabrics knitted from fine filaments have higher vertical deviation, i.e. greater height difference of low and high surface points, also contributing to rougher texture. In conclusion it can be stated that the chosen cost-effective method for determining fabric roughness can give an adequate representation of the fabric texture.

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Keywords: image analysis, knitted fabric roughness, texture.

TE P-2

THERMAL ABSORPTIVITY OF KNITTED FABRICS

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Clothing comfort describes the individual’s satisfaction with the physiological, psychological, and physical balance among the person, his/her clothing, and the environment. Thermal comfort properties, a subset of clothing comfort, are among the most important features of textiles. Within these properties thermal sensation can be expressed through the value of thermal absorptivity - an indicator of the ‘warm’ or ‘cool’ feeling upon the first brief contact of the fabric with the human skin. Factors that affect warmness/coolness can be largely categorized into fibre (cross section and moisture sorption), yarn (twist level, linear density and hairiness), and fabric properties (fabric density, thickness, weight, bulk density, porosity, and surface characteristics).

In this study, the effect of filament count on the thermal absorptivity of polyamide knitted fabric was investigated. A set of samples in single jersey knit with yarn count ranging between 17 dtex and 78 dtex were produced. Filaments were knitted in three different tightness levels, resulting in varying stich density of the finished fabric, developing three groups of samples. Thermal absorptivity of the fabrics was measured by the Alambeta instrument according to ISO 8301 standard. The measurements were repeated 5 times on randomly chosen parts of the fabrics, and average values and standard deviations were calculated. All measurements were conducted in a laboratory at a temperature of 21 ± 0.5 °C and 50 ± 1 % relative humidity.

The thermal absorptivity values depend on the thermal capacity and conductivity of the fabric and on the contact area of the skin and surface. The thermal absorptivity of samples ranged from 77 W $s^{1/2}$ K^{-1} m^{-2} to 155 W $s^{1/2}$ K^{-1} m^{-2}. The results indicate that the thermal absorptivity of samples increases with the growth of linear density and the cover factor. The surface character of the fabric greatly influences this sensation. A smoother surface increases the area of contact and the heat flow, thereby creating a cooler feeling. Coarser filaments distribute more evenly on the fabric surface, making the knitted fabrics cooler at touch.

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Acknowledgements: The authors would like to thank the Visegrad Fund for supporting cooperation between the Universities involved in this research via the Visegrad Scholarship mobility program.

Keywords: image analysis, knitted fabric roughness, texture.

TE P-3

ELECTROPHYSICAL PROPERTIES OF NONWOVEN VISCOSE/POLYPROPYLENE FABRICS

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Textile materials like woven, knitted and nonwoven fabrics are good insulators with very high electrical resistance. It is known that dielectric properties (effective dielectric permeability, electrical conductivity, and dielectric loss tangent) and electrical resistivity (volume resistivity and surface resistivity) of fabric are depending on several factors such as fiber type, fabric structure, moisture content of the material, air humidity, temperature, etc. The purpose of this investigation is to study the influence of the different content of viscose and polypropylene as well as the type of web bonding on the dielectric loss tangent and volume electrical resistivity. Also, the dielectric loss tangent was analyzed over a range of frequencies from 30 Hz to 140 kHz. Three investigated nonwoven fabrics were mechanically and thermally bonded, and one of the samples was additionally chemically bonded. The investigations were realized at 40 % relative air humidity.

Conducted analyses show that at frequencies below 100 Hz all investigated samples have higher, while at higher frequencies, the investigated samples show lower values of loss tangent. Namely, gradually decrease of the loss tangent value with the increase in the frequency from 30 Hz to 140 kHz was registered. The highest loss tangent value shows the sample with the highest viscose fiber content and thus the highest number of polar hydroxyl groups. The smallest loss tangent value was registered for a sample which was additionally chemically bonded.

Results obtained for the volume electrical resistivity was in accordance with the loss tangent values. The lowest resistivity value was recorded for sample with the highest viscose fiber content both in the machine direction as well as in the cross direction (5.27 GΩ·cm and 5.03 GΩ·cm, respectively), while the highest resistivity value was registered for additionally chemically bonded sample also in both investigated direction (11.84 GΩ·cm and 12.51 GΩ·cm, respectively). Some little differences in volume electrical resistivity in the machine and in cross direction are probably due to the fiber orientation in the samples and the number of contacts established between the fibers, because better contact between fibers causes an easier flow of charge.

Acknowledgements: Authors are grateful to the Ministry of Education, Science and Technological Development of the Government of the Republic of Serbia for funding the study under the Projects (OI 171029 and OI 172029).

Keywords: viscose/polypropylene, dielectric loss tangent, volume electrical resistivity, nonwoven fabrics.

TE P-4

CORRELATION BETWEEN CERTAIN SEWING THREAD CHARACTERISTICS IN KNITWEAR INDUSTRY

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The characteristics of seams on clothing will largely depend on the characteristics of sewing threads. Therefore, when choosing a thread, particular attention should be paid to the synergy of the characteristics of the threads to be matched to the characteristics of the material sewn. Together with the choice of seams, weaves and other technological parameters, the sewing threads need to provide the elasticity of the clothes when worn to offer unobstructed body movements. Depending on the purpose, it is difficult to systematize the properties of the threads in the order of importance. Obviously, they must possess the appropriate strength, elasticity, uniformity, smoothness, twist, yarn length count - thickness and raw material composition corresponding to the knitwear material, resistance to high temperatures, durability of coloration, balance and so on.

In this paper, analyzed are sewing threads of different yarn length counts and compositions intended for joining parts of garments from knitted fabrics. According to the obtained values of the test results, the threads of mixed polyester and cotton fibers have the advantage of joining garment parts. This advantage is due to elastic characteristics of their structural solutions. Also, in the paper are given the correlation relations (dependencies) of the individual characteristics of the threads which affect their use (breaking force, breaking strain, breaking force in the loop, breaking strain in the loop, yield strength, yield point, yarn length count, twist, etc.). Correlation equations have shown that they describe sufficiently well the connection between the characteristics of the threads. The engineers who are engaged in the design and production of sewing threads of different purposes can make good use of the obtained results and proposed correlation equations.

Acknowledgements: This work is a part of the research project No. TR – 34020, financed by the Ministry of Education, Science and Technological Development of the Republic of Serebia.

Keywords: correlation, breaking force, breaking force in the loop, yield strength.

TE P-4

INVESTIGATION OF THE AIR PERMEABILITY THROUGH THE KNITWEAR INTENDED FOR THE PRODUCTION OF SPORTSWEAR

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With the development of technology and an increase in living standards, requirements related to textile materials are changing.Today, is expected from clothing to complete a set of requirements, primarily related to their purpose.These requirements firstly relate to their functionality, comfort and aesthetics.This refers mostly to clothing intended for sport activities.When projecting sportswear, it is necessary to pay attention to its physiological characteristics, such as heat properties, humidity transfer and air permeability through the system; body - clothing - environment.These characteristics depend on the applied raw materials, types of yarn, applied interlacing, etc.However, layered dressing should be taken into account during sports activities (for example underwear and upperwear).In this case, when designing sportswear, all the materials through which the transport of moisture or air is carried out, and the performance of the clothes will depend on the combinations of all the materials constituting the system.

This paper presents the results of air permeability,both for individual knitwear of different raw materials, structural characteristics and different purposes (for laundry, t-shirts and upper garments), as well as for combinations of these materials in cases of layered dressing.

The obtained results can be used in projecting sportswear and to investigate the thermo-physiological properties of combination of materials for sportswear.

Keywords: physiological characteristics, air permeability, knitwear, sportswear.

Education (Ed)

Ed O-1

TEACHING CHEMISTRY USING INQUIRY LEARNING SPACE BY GO-LAB

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The new era of digitalization imposed the need for teachers to change their pedagogical approach in teaching students. Go-Lab is a great example that follows the trends of new pedagogical approaches of inquiry-based learning [1] by using digital technologies.

To use the possibilities offered by Go-Lab, students should follow an online link that takes them to the platform at http://graasp.eu/ where the lesson is posted, containing all the elements of the scientific research [2].

1) Introduction – getting to know the problem they need to explore by seeking information
2) Conceptualization – based on the information they have obtained, by formulating a hypothesis, they make assumptions which will be further explored in the next step.
3) Experimentation – students perform the experiments in virtual laboratory. They write down their observations using the observation tool.
4) Conclusion – based on the data obtained, students make conclusions and make comparison with the hypotheses.
5) Discussion – using the Padlet Application students have the opportunity to exchange data, conclusions and discuss mutual differences.

Since students are skillful when it comes to using digital technologies, these activities are very interesting for them. In this way, not only that their conceptual knowledge and investigation skills are developed but get an excellent substitute for experimental work for lessons related to STEM. By applying inquiry based leaning students develop and improve, skills such as critical thinking, problem solving and digital literacy.

Another excellent opportunity offered by Go-Lab is the ability to prepare Inquiry Learning Space (ILS) in native language that additionally facilitates the work of teachers who do not have good English language skills as it is easier for them to used it.

The Go-Lab federation of online labs opens up virtual laboratories (simulation), remote laboratories (real equipment accessible at distance) and data sets from physical laboratory experiments (together called “online labs”) for large-scale use in education. In this way, Go-Lab enables inquiry-based learning that promotes acquisition of deep conceptual domain knowledge and inquiry skills, with the intent to engage students in pursuing a career in science. For students, Go-Lab offers the opportunity to perform scientific experiments using online labs, in pedagogically structured learning spaces. Go-Lab’s ILSs give structure to the students’ inquiry process through an inquiry cycle. It gives students guidance, where dedicated (and connected) scaffolds for inquiry processes play pivotal role. Teachers can create and adapt to the inquiry learning phases and the associated guidance in an ILS, through a simple wiki-like interface where they can add scaffolds and tools to ILS using a straightforward drag and drop feature.

Teachers can also adapt scaffolds and tools (e.g. change the language or the concepts available in a concept mapper) through an “app composer”. When creating ILSs, teachers are supported by scenarios and associated defaults ILSs that can be used as a starting point for development. Thus, it is important to support and encourage teachers to use the default ILSs as a source of inspiration [3] and to provide as many as possible good examples of ILSs thus foster teachers’ collaboration.

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Keywords: chemistry education, digital technologies, Go-Lab, inquiry-based learning, Inquiry Learning Space, online labs.

Ed P-1

GOOD PRACTICE EXAMPLES OF TEACHING CHEMISTRY USING ONLINE LABS

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Teaching chemistry is often challenging and complex process that involves constant improvement of teachers' competences leading to high quality educational process. The teaching profession has a crucial role in the society. Teachers must be professionals in their field and seek out new and improved techniques related to their field of interest. For that purpose, a teacher needs to have a solid pedagogical content knowledge that involves both content knowledge and pedagogical skills [1,2]. The chemistry curriculum [3] implies a well-equipped laboratory and inquiry-based activities for successful realization of teaching goals. Practical work [4] has a central and distinct role in chemistry education, and chemistry is almost exclusively, one could 'engage' all five senses of a student [5].

Unfortunately, this is not the case in Macedonia and not all of the experiments are possible to make. Therefore, teachers and educators need to develop additional teaching strategies. Anything where the students are actively involved in developing their own learning is a potential learning activity. A good practice that teachers could benefit of is using online labs in chemistry lesson as substitute for practical work. Thus, the lesson is set on the Graasp platform (http://graasp.eu), which is an authoring space of the Go-Lab Authoring Platform [6]. This platform enables teachers to easily create Inquiry Learning Spaces, which are virtual spaces, structured according to the phases of the inquiry learning process and containing online labs, inquiry learning applications, and any other multimedia learning materials selected by the teacher. These spaces can be shared with his/her students, so they can study individually or in groups, going through all steps of a research process and conducting online experiments. Moreover, using the learning analytics applications, the teacher can monitor the progress of the students and provide support, if needed. Communication and collaboration tools for teachers and students are available as well.

A good practice example was developed by the authors following the inquiry-based learning approach. The lesson was aimed to help students learn how to measure pH of the various solutions by using virtual pH meter and to understand how pH values change after adding a certain amount of water. It is interesting that most students assumed that the addition of water in all solutions would lead to an increase in pH values. But thanks to this virtual laboratory and virtual pH meter they came to a different result that helped them gain scientific knowledge.

One of the limitations of this approach is the computer and internet requirements but given the fact that most students use smartphones and internet, very soon this obstacle will be overcome. It is believed that this approach improves both the teaching and learning process, thus the authors are challenged to encounter the idea of using online labs for educational purposes and to try to include as many teachers as possible from different background. Furthermore, we attempt to develop more online lessons and to popularize these good practice examples among teachers.

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Keywords: chemistry curriculum; chemistry education; Go-Lab; inquiry-based learning; Inquiry Learning Spaces; online labs; pedagogical content knowledge.

Ed P-2

APPLICATION OF INTERACTIVE FORMS OF TRAINING AND ASSESSMENT IN THE DISCIPLINE "TECHNICAL SAFETY AND NATURAL DISASTER'S PROTECTION"

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The education has nowadays, dual key role, both social and economic, and the demands to its improvement are continually increasing. On topics such as Technical safety and natural disaster's protection that are so vital and constantly changing, it is necessary to continuously incorporate new teaching / learning methods. In this way, learners will be able to acquire the necessary competences and a wide range of key competences for acquiring information, its use in decision-making and its implementation in practice.

The present work shows how to apply interactive learning in the teaching and testing of knowledge in the discipline " Technical safety and natural disaster's protection" of the students from University "Prof. d-r Assen Zlatarov" in Burgas, Bulgaria, as an opportunity for the student to become a full participant in the learning process and his / her experience and ability to take decisions on this basis, serve as a major source of learning knowledge. To reach this goal, the work team has developed an application to use the latest Google technologies to create test-based assessment materials for the discipline, providing a wide variety of questions and answers. Each of them can be played at random, and the results can be visualized both in text and graphically. The answers of each student individually and all together can be considered together with the aim of generating summary results. The test thus developed can be activated and then disactivated, more than one test can be accepted, and besides objective assessment of the knowledge, it also enables the student to make decisions in an interactive environment.

Acknowledgements: University "Prof. d-r Asen Zlatarov", Burgas, Bulgaria.

Keywords: technical safety, interactive training.

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