

**Сојуз на хемичарите и технолозите  
на Македонија**



**Society of Chemists and Technologists  
of Macedonia**

**22<sup>nd</sup> Congress**

with international participation

**BOOK  
of  
ABSTRACTS**

Sept. 05 – 09 2012  
OHRID  
Metropol Lake Resort



**The 22<sup>nd</sup> Congress was organized by the  
Society of Chemists and Technologists of Macedonia  
member of EuCheMS**



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## Welcome Address

Dear Participants,

The 22<sup>nd</sup> Congress of the SCTM (*Society of chemists and technologists of Macedonia*) is a continuation of a traditional gathering of experts in chemistry, chemical technology and allied fields from Macedonia and other countries. This manifestation is organized biennially by the SCTM for near half a century.

Again this September we will enjoy the pleasure to hear science from a choice of invited lecturers, and to understand what is new in the fields of chemistry, chemical engineering, metallurgy, pharmacy, agriculture, etc. We will also read the posters with results of research done in the past two years by our colleagues and young scientists that grow up in our faculties, institutes and industry.

This Congress is not a modest one. More than 300 abstracts were submitted for presentation from almost 240 authors of 12 countries. A total of 20 lecturers, plenary, sectional and key-note ones are expected to present their lectures.

You are aware that in a year with economic crisis it is not an easy task to organize a Congress of this size. Thanks to our sponsors, as well as to the support by OPCW, our Congress will take place the same way as the previous ones. Your interest is also an important element for this success.

The Congress is scheduled to cover four days and also to offer possibility to visit some of the historical sites and touristic attractions that the ancient Ohrid has. We do hope that you will keep it in your memories by its scientific highlights, cordial hospitality and great friendship.

Thank you for attending the 22<sup>nd</sup> Congress,

President of SCTM,

Prof. Svetomir Hadzi Jordanov



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- PE-15 Stoyanka Christoskova, Ivelina Stoyanova, Dimitar Dimitrov, Maria Stoyanova, Maria  
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- PE-16 Slavica Grujić, Kiril Lisichkov, Igor Pandzic,  
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- PE-17 Kiril Lisichkov, Stefan Kuvendziev, Mirko Marinkovski, Dejan Dimitrovski, Vasilka  
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- PE-18 Kiril Lisichkov, Stela Conic, Radoslav Grujic, Mirko Marinkovski, Stefan Kuvendziev,  
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- PE-19 Aleksandar Aleksovski, Samra Saletovic, Midhat Jasic, Emilija Spaseska Aleksovska,  
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- T-10 Maja Nofitoska, Goran Demboski,  
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- T-11 Jelena Mitic, Radica Nicic, Dragan Djordjevic,  
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**PLENARY LECTURES (PL)**

## PL-1

# EXAMPLES OF SYNERGY LEADING TO INNOVATIONS IN MATERIALS SCIENCE

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Faced with the challenges of the 21<sup>st</sup> Century, new and exciting opportunities have arisen and these include preparation of new materials with interesting properties, novel coatings, recycling of materials, capturing of carbon dioxide and, generally, better, less polluting and more energy efficient methods of metal extraction. As well as solving technical problems, it is also possible to create ideas that can attract financial support to create new ventures. This presentation is concerned with the translation of science into viable commercial products in an academic environment. It will be shown that by combining knowledge from materials science, physics and chemistry combined with experience of industrial problems, it is possible to devise solutions which are able to attract funding, not only for the underlying research but, also, to start spinout companies, thereby, eventually creating wealth and employment. A wide range of problems and solutions will be discussed and these will include the generation of carbon nanotubes from graphite and their incorporation into lithium ion batteries in order to increase the capacity of the batteries. Novel methods for the extraction of metals which include the development of inert anodes which allow the evolution of oxygen rather than carbon dioxide. Sensors for the detection of hydrogen and other elements and, finally, the use of electrochemistry to generate oxygen for wound healing. Finally, examples of technology transfer of these ideas to University spin-outs and existing companies will be presented.

## PL-2

### LOADED NANOFIBERS FOR SAFETY AND SECURITY

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The objective of this investigation to develop a systematic and progressive methodology to develop micro/nanofibers using electrospinning employing ceramers and other novel materials mixed in solutions of high-performance polymers. The methodology involves identification and selection of novel combinations of loading and high-performance polymers. The resulting nano/microfibers with properties leading to increased mechanical strength, improved sensitivity to contaminants, better filtering capabilities, improved response to electromagnetic stimuli, and desired conductivity. Also, high surface area/volume ratio and fibers with varying functionality, combined with its potential biocompatibility and biodegradable nature, offers tremendous promise for diverse applications in tissue engineering, targeted vaccine delivery, non-thrombogenic materials for blood contacting applications, chemical and biological sensors, system-on-fibers (SoF) and e-textiles.

Such characteristics will allow for the creation and improvement of barrier materials for force protection, embedded informational and communication technologies (ICT) devices - signal receiving/communication capability, sensors that respond to environmental contaminants, built-in timed-release or physiological condition based-release therapeutics, filtering of contaminants, biological mimicking for sensing, and optical cloaking – all of which promise direct applications of loaded micro/nano fibers in outerwear used in combat theatre.

In addition, a selected application of the loaded electrospun nanofibers in biomedicine will be presented.

It was shown that antibiotic loaded biodegradable and biocompatible polymeric electrospun nanofibrous membranes can prevent post-surgery induced intra-abdominal adhesions by providing a physical barrier during wound healing process and at the same time a functional barrier against strains of microorganisms thereby reducing the local inflammatory response. The results of our previous studies including synthesis of biocompatible and biodegradable polymers, production and characterization of electrospun nanofibers from those polymers, their loading with drugs and the release of the drugs from the produced matrices would provide a linkage for the development of new functional barriers for protection applications.

The work is complemented by using advanced science convergence methodologies such as automated data analysis, mining and surveillance (ADAMS<sup>TM</sup>) and technology foresight and road-mapping (TechFARM<sup>TM</sup>) to provide additional knowledge base. Preliminary data of fibers using loaded high performance polymers will be presented with the objective to fabricate ceramers embedded multi-functional nano/micro fibers for military outerwear and gears that provide an integrated solution path through a revolutionary approach of using ceramers embedded in high performance polymers as materials for suits, masks, and embedded sensors.

Keywords: e-spin, nano-fibers, filtration, mechanical strength, sensors

## PL-3

### PERSPECTIVE TECHNOLOGIES FOR BIODIESEL PRODUCTION

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During the past decades energy demands have been increasing due to industrialization and the human population growth. The primary energy source worldwide has been fossil fuel, which limited reserves lead to the increase of fossil-based fuels price and could cause world energy crisis. Combustion from fossil fuels is major source of atmospheric pollution and greenhouse gases emission. Therefore, the substitution of fossil fuel with renewable, clean energy is seriously considered, and the main alternative to fossil fuel is biodiesel.

Biodiesel is defined as the monoalkyl esters of long-chain fatty acids derived by the alcoholysis of vegetable oil or animal fats and alcohol. Conventionally, biodiesel is obtained by methanolysis of edible vegetable oils in the presence of a homogeneous base catalyst. The advantage of this process is achieving the high methyl esters yield under the mild reaction conditions. However, major problems refer to handling a variety of different feedstocks and to removal of these catalysts, which is technically difficult. The higher amount of water used in washing and consequent treatment of the resulting effluent added to the overall process cost.

Therefore, much recent research has been focused on developing methods to reduce the biodiesel production cost. The use of heterogeneous catalysts significantly simplifies the process of separation and purification of the products, reduces environmental problems, allows reuse of the catalyst and contributes to positive economic effect. Using wastes as raw materials for catalyst synthesis could eliminate the wastes and simultaneously produced the catalysts enabling sustainable process development. The use of cheap and efficient catalyst makes the process economic and fully ecologically friendly. Based on environmental benefits, the enzyme-catalyzed process (called “green process”) is expected to be widely used in the future. Different intensification methods such as ultrasonic and microwave irradiation, hydrodynamic cavitation, addition of co-solvents and application of supercritical synthesis conditions have been tried out to improve the biodiesel production process. Among these methods is also the development of novel reactor types that improve the performance of the reaction.

Keywords: alcoholysis, biodiesel, heterogeneous catalyst, intensification methods

**PL-4****ELECTRON SPIN RESONANCE – A POWERFUL SPECTROSCOPIC  
TOOL IN CHEMICAL, BIOLOGICAL AND MEDICAL STUDIES**Bui N.N.<sup>1</sup>, Pasioka B.<sup>1</sup>, Bogeski I.<sup>1</sup>, Gulaboski R.<sup>2</sup>, Mirceski V.<sup>3</sup>, Hoth M.<sup>1</sup>, Kappl R.<sup>1</sup>

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Electron Spin (Paramagnetic) Resonance (ESR or EPR) is the method of choice to study paramagnetic molecular systems containing unpaired electrons with high selectivity and sensitivity. Because of these properties, radicals or transition metal centers involved in chemical reactions, in biological processes as well as in cellular or tissue systems become accessible to a detailed analysis.

Quinone compounds are an important class of substances in chemistry but also play an essential role in electron transfer processes in biological systems. We have studied the hydroxylation reactions of partially and fully substituted para-benzoquinones with two methoxy moieties as models for the naturally occurring quinones (e.g. Q10) with a variety of methods including UV-Vis, voltammetry, and nuclear magnetic resonance. In particular, with ESR the formation of various quinone radicals and their transformations in aqueous alkaline solutions could be observed. The spectral patterns allowed identifying the molecular radical species and to follow the kinetics of the radical transformation. We show that also fully substituted para-benzoquinones are hydroxylated at the methoxy positions yielding compounds with interesting new and physiologically important features such as the ability to bind divalent ions (like Ca<sup>2+</sup>) and having strong antioxidative properties.

A further project employs the EPR spin trapping/monitoring technique to follow the evolution of the primary superoxide radical production by human CD14<sup>+</sup> monocytes (MCs) which belong to the human innate immune response system. The superoxide radicals O<sub>2</sub><sup>•-</sup> are generated by NADPH oxidase (NOX) which transfers electrons sequentially from NADPH to molecular oxygen. Because of the short life time, the superoxide radical has to be kinetically stabilized by spin traps. We performed studies with sensitive redox activated hydroxylamine spin traps (such as CMH). Cyclic voltammetry was applied to understand the redox properties of CMH and its interaction with superoxide and redox active additives. It was possible to quantitatively determine the radical production of MCs and to analyse the effects of inhibitors of NOX relevant for clinical application and of antioxidants such as ascorbic acid and hydroxylated quinone compounds.

Key words: Electron Spin Resonance, quinone, superoxide

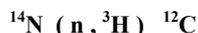
## PL-5

## ENVIRONMENTAL OXYGEN AND HYDROGEN ISOTOPES IN THE HYDROLOGICAL CYCLE - Principles and Applications

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The need for freshwater is one of the most important issue facing mankind today especially having in mind that problems associated with it affect the lives of many millions of people, round the world. More water and with a better quality can not be acquired without the continual and extension of hydrological research. In this respect IAEA's program in nuclear applications over the last five decades has contributed a lot in the development and practical implementation of isotope techniques and methodologies related to the research, assessment and management of water resources. Isotope studies applied to a wide spectrum of hydrological problems related to both surface and Groundwater resources as well as environmental studies in hydro-ecological systems are presently an established scientific discipline, often referred to as "Isotope Hydrology". That is why, Nuclear techniques which are among the recent technological developments have already confirmed their contribution to a better understanding of many hydrological phenomena round the world. However, beside the wide range of techniques including the use of nuclear instruments and injected tracers, hydrologists also had to use a group of techniques based on the natural variations of environmental isotopes in waters of the hydrological cycle, providing useful information on many hydrological questions and dilemma. At present, beside the commonly used radioactive isotopes of tritium (H-3), (as does  $^{14}\text{C}$ ) from a nuclear reaction between atmospheric nitrogen and thermal neutrons (Libby, 1946),



and carbon(C-14), application of environmental stable isotopes of deuterium and oxygen-18 as a tool has been unavoidable especially in regional hydrological investigations that we have performed during the last 20 years. This might be simply explain by the fact that differently from all artificial tracers which are present in dissolved form and therefore, are subject to loss by precipitation, adsorption and exchange, these isotopes except C-14 are part of the water molecule and represent the only real available water tracers.

Deuterium and Oxygen-18 occur in the ocean waters in concentrations of cca 320 ppm and 2000 ppm for the molecular species of HDO and  $\text{H}_2^{18}\text{O}$ , respectively. As for the practical purposes it is not necessary to determine their absolute value, the isotope ratios of D/H and  $^{18}\text{O}/^{16}\text{O}$  with respect to an internationally accepted standard are measured in a mass spectrometer. The isotope data are expressed as delta ( $\delta$ ) units in per mil (‰) according to :  $\delta = (R - R_{\text{SMOW}} / R_{\text{SMOW}}) 10^3$ , where, R and  $R_{\text{SMOW}}$  are the isotopic ratio ( D/H or  $^{18}\text{O}/^{16}\text{O}$  ) of the sample and the SMOW (Standard Mean Ocean Water) standard, respectively. Due to the difference in water pressures in air of the different isotopic species of water, fractionation takes place as a parallel process always when water changes its state. With respect to the liquid phase, water vapor is depleted in the heavy isotopic species. This isotopic depletion is higher with increasing of the latitude, distance from the sea and altitude. Seasonal variation of heavier isotopes with increased values during the summer period is evident. In this sense, with an aim to determine the origin of the water of several Springs (St. Naum-Ohrid, Rasche-Skopje and others) as well as the local hydrological relationship, relevant Isotope Techniques have been applied and respective ages/MRT (Mean Residence Time) obtained, a part of which more in detail will be presented by Anovska-Jovcheva et al., on this Congress, as well.

Key words : environmental hydrogen and oxygen isotopes, hydrological cycle, recharge zones and ground water age

**INVITED LECTURES (II)**

## IN-1

# LASER-INDUCED PREPARATION OF ENCAPSULATED METAL NANOPARTICLES

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There is great interest in synthesis of magnetic nanoparticles, which is due to their many promising applications (e.g. magnetic inks, isolating systems, recording media, magnetic carriers and magnetic resonance imaging in medicine). The particles are, however, easily agglomerated and oxidized and must be therefore stabilized by insulating shells of polymer, silica, glasses or carbon.

Decomposition of the gaseous acetylene – metal carbonyl mixtures induced by a single ArF laser pulse is a very efficient and novel method for formation of metal nanoparticles completely covered with amorphous carbon shell. The particles are formed by dehydropolymerization of acetylene catalyzed by an *in situ* generated metals. The encapsulated and stabilized iron and cobalt nanoparticles and iron/cobalt nanostructured alloys were prepared from iron pentacarbonyl and cobalt nitrosyl tricarbonyl.

The properties of the metal (core) - carbon (shell) nanocomposites were examined by X-ray photoelectron, infrared and Raman spectroscopies, by electron microscopy techniques and X-ray diffraction. In this inexpensive process, formation of copious amounts of carbon encapsulated metal nanoparticles is efficiently achieved and the carbon/metal ratio as well as the size of the core and shell is controlled by reaction parameters. We also report on thermal properties of these particles and on structural changes they undergo at high temperatures. Magnetic measurements show increased saturation magnetizations as a consequence of complete encapsulation of the metallic core. The complex structure of the encapsulated nanoparticles was elucidated by means of the Moessbauer spectroscopy at room and low temperatures.

Keywords: Iron/cobalt nanoparticles, carbon encapsulation

## IN-2

**FROM STRUCTURE TO FUNCTION: TOWARDS AN ATOMISTIC UNDERSTANDING OF THE ACTION OF ADDITIVES RELEVANT FOR THE DAMASCENE AND TSV COPPER PLATING**Flügel<sup>1</sup>, M. Arnold<sup>1</sup>, D. Mayer<sup>1</sup>, N.T.M Hai<sup>2</sup>, F. Simona<sup>2</sup>, M. Cascella<sup>2</sup> and P. Broekmann<sup>1,2</sup>

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Copper electrodeposition is of paramount importance for today's fabrication of integrated circuits. The fill of small, nm-sized Damascene features and the fill of large,  $\mu\text{m}$ -sized Through Silicon Vias rely both on the super-conformal growth of copper involving an "accelerated" copper electrodeposition at the feature bottom with respect to the "suppressed" deposition at the wafer surface and the upper side walls of those features. Such non-uniformity in the local reaction velocity is typically achieved by the non-uniform distribution of suppressor additives and their specific antagonists inside and outside the feature. Transport and adsorption kinetics in combination with shape evolution phenomena at the feature bottom have been identified as physical origin for the required non-uniformity in the local additive surface coverage. Successful superfill is achieved only when the non-uniformity in the additive surface coverage is maintained over the complete fill process. Considering the different time-scales in the processing of sub-50nm Damascene features and  $\mu\text{m}$ -sized 3D-TSVs it appears crucial to take the time dependence of the structural stability of those suppressor ensembles into account.

It is the general aim of this contribution to discuss different strategies from chemistry and electrochemistry side in order to achieve such non-uniformity in the surface additive distribution tailored for different time scales. Suppressor concepts commonly used for Damascene processing are typically not well suited for 3D-TSV plating due to the temporal instability of the PEG/Cl suppressor ensemble. The time-scale of the PEG/Cl deactivation from electrolyte side is too short for the 3D-TSV plating. It is the particular aim of this contribution to discuss alternative plating routes towards superfill effects for 3D-TSV plating that rely on chemistries taking advantage of anion-cation pairing effects, hydrophobic interactions and Cu(I) coordination chemistry. A molecular scale understanding of the complex additive surface chemistry is achieved by a combination of in situ STM, XPS, chronopotentiometry, DFT and cross-sectional FIB.

Keywords: electrodeposition, copper, integrated circuits, nano-sized material.

## IN-3

# SPUTTERED THIN FILMS AS CATALYSTS FOR HYDROGEN ENERGY CONVERSION

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Hydrogen energy systems with a proton exchange membrane electrolyte (PEMHES), including hydrogen generators/electrolysers, fuel cells, and reversible bifunctional devices have received significant attention in the recent decades due to their high efficiency and environmental compatibility. They have shown great potential as alternative power sources, particularly for stationary power generation and transportation applications due to their low operating temperature, fast start-up, high power density, and low emission of pollutants. Nevertheless the achieved substantial progress however, the PEMHES are not broadly utilized because their cost and durability are still not satisfactory. Therefore, the research in the field is focused on development of novel catalysts with increased catalytic activity and sustainability to degradation. In addition to performance improvement, a decrease in catalytic loadings combined with better catalyst utilization is highly desirable in order to achieve commercially acceptable cost reduction for these otherwise very attractive energy systems.

The method of magnetron sputtering is a feasible technique for preparation of thin films with controllable thickness and tailored properties (composition, density, porosity, etc.) It produces compact mono, bi- or poly-metallic and/or oxide films upon a selected substrate material or even directly onto the polymer membrane and is easily adoptable for direct incorporation of the catalytic material into the matrix of the membrane electrode assemblies (MEA) used in PEMHES. This work summarizes the results on deposition of various thin sputtered films (noble metals, alloys, metal oxides and multilayer structures) and their characterization in view of structure, morphology and electrocatalytic efficiency toward the partial electrode reaction proceeding in PEMHES. The developed materials demonstrate high catalytic activity combined with long-term mechanical stability and corrosion resistance. The results obtained give credence to consider the method of magnetron sputtering as a reliable and cost efficient alternative method for catalyst preparation.

Key words: hydrogen, fuel cells, exchange membrane electrolyte, magnetron sputtering.

## IN-4

# CURRENT RESEARCHES AT ICTP-CNR ON NANOTECHNOLOGY APPLICATIONS TO FOOD PACKAGING

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This lecture will be divided in two parts. In the first the state of the art of the applications of the nanotechnologies to food packaging sector in terms of materials, additives and processes used for compounding and/or structuring will be illustrated and most recent and important examples of nanopackaging will be also examined.

In the second part recent results concerning innovative nanocomposite systems prepared and characterised at ICTP-CNR that could find applications in food packaging industry will be shown.

The following ICTP studies on food packaging polymeric-based systems will be described:

- Biodegradable starch/clay nanocomposite films;
- Polypropylene modified with calcium carbonate nanoparticles;
- Polyethyleneterephthalate filled with modified calcium carbonate nanoparticles.

The structure, thermal and mechanical characteristics of the nanocomposites as well barrier properties will be analyzed. Moreover, food-contact tests with food and simulants have been performed in order to study the possibility of utilising these materials in the food packaging sector.

Finally some considerations on the migration of nanoparticles from packaging materials to foods together with environmental implications of the use of these materials, considering their entire life cycle, will be also discussed.

Keywords: nanocomposites, active and smart packaging, food.

## IN-5

# ON USE OF THE WIENER INDEX IN STUDY OF GRAPHENE AND OTHER NANOSTRUCTURES

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Although being the oldest topological index, the Wiener index is still used by many mathematical chemists. Recently this index has been extensively applied to study carbon nanostructures from fullerenes and nanotubes to graphene. Some of the obtained results will be reviewed.

It will be shown how the Wiener index can be used in topological modeling of fullerenes, nanotubes and graphene. Properties of graphene and its derivatives fascinate scientists and have already found various practical applications with expectations for graphene to become material of many future technologies. A special attention is given here to topological modeling of defects drifting in graphene. Rearrangements of graphene are studied by applying iterated Stone-Wales rotations. A topological analysis provides information on relative chemical distribution of pentagon-heptagon pairs, the 5/7 defects, diffusing in graphene layer. The related computations are performed in dual topological space with the Wiener index being taken as a topological potential that governs the migration of defects through graphene layer.

The aim of the presentation will be to show that topological modeling based on the use of the Wiener index is able to simulate complex mechanisms in large structures like diffusion of defects in graphene layer and so quickly point to interesting structures for subsequent *ab initio* studies.

*The results to be presented are obtained in collaboration with A.R. Ashrafi, F. Cataldo, M.V. Diudea, F. Ghorbani, A. Iranmanesh, O. Ori and D. Vukicevic.*

**Keywords:** graphene, 5/7 structural defects in graphene, fullerenes, C66 fullerene, Wiener index, topological modeling by Wiener index

**IN-6**

**PECULIARITIES IN THE SINTERING BEHAVIOUR AND THE PHASE  
FORMATION OF CERAMICS FROM PRETREATED MSWA**

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New opportunity for a total removal of the fluxes in traditional ceramics by usage of huge amount of secondary raw materials (SRM) is highlighted. Two kinds of pretreated bottom ashes from municipal solid waste incinerator (MSWA) and three different industrial clays are combined in order to obtain six different ceramics with 40 wt% clays and 60 wt% SRM from MSWA. The phase transformations and the sintering behaviours of these innovative ceramic batches are studied by non-isothermal DTA-TG, hot stage XRD and non-isothermal optical dilatometry. After that, the optimal sintering temperatures and times for each batch are evaluated with precise isothermal dilatometric measurements. It is demonstrated that the sintering behaviour and the final phase composition of the new ceramics can be explained by the position of their chemical composition in the phase diagram  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ . Best results were obtained by using refractory clay. In this case, semi-industrial tests were performed and the chemical, mechanical and technological properties of the obtained specimens were studied. It was demonstrated that, due to formation of high amount of anorthite solid solution during the sintering and cooling steps, the samples show structures similar to one of the glass-ceramic materials resulting in elevate mechanical characteristics.

Key words: industrial wastes, ceramics, sintering, phase formation, mechanical properties.

## IN-7

### **COPPER METALLURGY IN THE REPUBLIC OF MACEDONIA: STATE- OF-THE-ART AND PERSPECTIVES**

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A survey is given of the copper metallurgy in the Republic of Macedonia, as far exclusively applied in the Bucim copper mine, ore dressing and flotation, that recently started to leach the accumulated mine overburden heap and to extract the copper metal by an electrowining process. This is the very first time copper to be completely produced, from ore ‘till the metal in the country.

Bucim mine is operating since 1979 and in the span of these more than 30 years the company did experience a number of transformations. The last and the most significant one took place in 2005 when it became part of the Russian SOLVEJ. Immediately the operation was restarted and modernized, while the environmental protection was improved. Soon a new investment cycle was initiated, aimed at closing the copper extraction process and in the same time valorization of the formerly disregarded copper bearing tailings. Next to the economic importance, this activity is of environmental benefit too, because it will finally end the spontaneous acid mine drainage that for a long period did contaminate the surface and groundwater in the region.

Heap leaching, followed by leachate treatment (concentration and purification) and electrowining units were constructed as part of the new plant.

Today the mine produces some 40.000 tones per year copper concentrate that gives 8.000 tones copper per year. The content of gold in the concentrate is 10-12 grams per ton. The new plant produces 2.400 tons cathodic copper per year.

Extensive geological research done in a period of years resulted in discovery of new copper bearing locations that deserve to be exploited. So, construction of new copper extraction plant is in course, aimed at utilization of the new fields in the region.

Key words: copper metallurgy, ore dressing, heap leaching, electrowining

**KEY-NOTE LECTURES (KN)**

**KN-1****SYNTHESIS OF NANOCOMPOSITES OF DIFFERENT ARCHITECTURES  
AND APPLICATIONS BASED ON COPPER, NICKEL AND ALUMINA**Željko Kamberović<sup>1</sup>, Marija Korać<sup>2</sup>, Zoran Andić<sup>3</sup>

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Considering that nanostructural materials are expected to have special physical and mechanical properties, in the recent years the examinations of synthesis and characterization of the nanocomposite system attracts even greater scientific interest. This paper presents production of sintered contacts materials produced from nanocomposite powders obtained by combination of thermochemical synthesis of Cu-Al<sub>2</sub>O<sub>3</sub> powder and mechanical alloying of atomized copper powder with previously synthesized Cu-Al<sub>2</sub>O<sub>3</sub> powder. Produced powders were characterized by X-ray diffraction and Analytical Electron Microscopy. Characterization of sintered samples included Scanning Electron Microscopy (SEM), Energy Dispersive Spectrometry (EDS), measurement of hardness and specific electrical conductivity. By thermochemical method of Cu-Al<sub>2</sub>O<sub>3</sub> nanocomposite synthesis, i.e. deposition from aqueous solutions, in combination with mechanical alloying, significant effects of reinforcement were achieved as a result of homogenous distribution of alumina in the nanocomposite system.

In combination with conventional methods, thermochemical process of nanocomposite powders synthesis could be successfully applied for synthesis of new nanocomposite catalysts, which are characterized by a high degree of dispersion of the catalytically active component, respectively the catalyst with high activity and selectivity. The high degree of dispersion is the result of uniform distribution of the catalytically active component into alumina suspension, realized during the thermochemical treatment in the synthesis of nanocomposite catalysts. In accordance with this, the paper shows the synthesis of Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-Pd/Al<sub>2</sub>O<sub>3</sub> nanocomposite catalysts with homogeneously dispersed Ni particles, as catalytically active component, and Pd, as activity modifier, supported on ceramic Al<sub>2</sub>O<sub>3</sub> based foam. Namely, the previous synthesized monolith was soaked in a mixed alumina suspension with NiCl<sub>2</sub>, PdCl<sub>2</sub> and appropriate organic additives in order to obtain a nanocomposite catalysts with homogeneous distribution of catalytically active components. Characterization of obtained Al<sub>2</sub>O<sub>3</sub> foam, as the active catalytic components primary carrier, and synthesized nanocomposite catalysts included SEM, EDS, gas permeability and mechanical properties.

Synthesis of nanocomposite materials with homogeneous distribution of particles on the nanometer level may lead to formation of new materials with improved or even unexpected properties.

Keywords: synthesis, copper, nickel, alumina, nanocomposite, contact materials, catalysts

## KN-2

### LASER INDUCED SYNTHESIS OF BINARY ALLOYS IN THE GAS PHASE

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A novel processes capable of producing a range of novel nanostructured metal alloys have been examined and optimized for formation of unique and yet morphologically unknown nano-structured alloy materials.

One process (i) is based on laser induced gas phase co-decomposition (IR laser co-thermolysis) of mixed precursors (consisting in clustering and intermixing of extruded metal atoms and rapid cooling of spontaneously formed nano-sized multiple-metal clusters and their agglomerates depositing from the gas phase).

The second one (ii) consists in highly focused radiation at the surface of solid metal target leading to the ablation/etching of metal atoms and inducing interaction with present gaseous reactant which is decomposed through laser induced dielectric breakdown. Simultaneously generated clusters of two different metals interact in the gas phase and they are deposited from the gas phase as nanostructured alloys.

The processes have been explored with selected volatile precursors (tetramethyltin, tetramethylgermanium, silane, germane, stannane) when clustering/coalescence events were challenging for fabrication of binary alloys with improved properties or for production of alloy materials from metals which are immiscible in the bulk. The techniques employed for the characterization of nanoalloys were FTIR, Raman spectroscopy, TGA, SEM, EDX, XRD, HRTEM, SAED.

Key words: laser decomposition, nanoalloys, gas phase synthesis, laser ablation, amorphous phase

### KN-3

## CONTEMPORARY INSIGHTS OF FOOD CHEMICAL INGREDIENTS TO THE EFFECTS OF HUMAN BODY HYPERSENSITIVITY

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Nowadays, increasing research focused to relationships between humans and food and implications arising from this relationship and reflect to human health. Foods that are consumed daily, except of macro and micro nutrients, contain many other ingredients that act on the human body by a variety of biochemical mechanisms.

The aim of this paper is to give an overview of food ingredients that cause various adverse effects on human body, to show significant methods for identification that reactions and on this base prevent their influence to diseases, using of elimination diets. The results presented in this paper obtained by compiling existing research.

The food hypersensitivity in the form of allergy, intolerance, aversion, and other diseases and symptoms is increasingly present in the population in industrialized and developing countries. Modern nutritional biochemistry and orthomolecular biology try to give answers to the adverse effects of food components to the human body. The most common hypersensitivity in the form of food allergies occur: milk, eggs, fish, crustaceans and shellfish, tree nuts, peanuts, wheat and soybeans, and the food products that contain them. However, adverse reactions of the organism in the form of hypersensitivity may occur in other ingredients such as unnutritious biologically active ingredients, pesticides and antibiotics residues, environmental contaminants, additives, residues of detergents, chemicals migrating group from packaging, microorganisms and their metabolites, products of food processing etc. The presence in traces of some of these food ingredients can cause adverse reactions. Many food ingredients during digestion and metabolism react with other metabolites that can cause reactions manifested in the form of hypersensitivity. The organism reaction may occur immediately after eating or with delayed response. Delayed reactions can cause a variety of chronic symptoms until the person is not detected and eliminated certain foods from your diet.

Because of that, today is developing a variety of chemical, biochemical, physical and biological methods to identify food ingredients that affect the adverse reactions, and methods to identify the mechanisms of adverse reactions in the body. A significant improvement in efficiency is achieved using biosensors, and one of the methods that are increasingly being used is based on bioresonance.

The development of food analytical methods as well the analysis of specific substances in the human body, created the possibility to define individual nutritional guides tailored to each person individually, in order to prevent hypersensitivity and other adverse reactions to food.

Key words: food ingredients, adverse reactions, hypersensitivity

**KN-4**

**IN-SITU REFLECTION ELECTRON MICROSCOPY OF (111) SILICON  
CRYSTAL SURFACE**

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Silicon crystals are still the main material for production of electronic components like memories, processor units, etc. Understanding the basic processes that occur onto a crystal is of great importance in order to obtain desired surface patterns. Reflection Electron Microscopy is unique technique aimed at in-situ observation of vicinal crystal surfaces at high temperatures. Together with a specially designed sample holder that controls the deposition flux, it allows application of different ambient conditions to the crystal surface – supersaturation, equilibrium or undersaturation. Main processes that will be presented at real time speed are crystal sublimation and crystal growth by step flow mechanism, destabilization of the crystal surface by a step bunching formation, single and double dislocation spiral growth, surface reconstruction transition (1x1)-(7x7), and pyramid like structures growth.

Key words: reflection electron microscopy, vicinal surface, step flow growth.

## KN-5

# COMPUTER-AIDED MODELING OF HORMONE RECEPTOR-MEDIATED TOXICITY

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Many chemicals that are widely used exhibit considerable toxicity due to the interaction with the receptors in the human body. Some of those receptors belong to the group of xenosensors and are activated in order to eliminate the chemicals from the system. Other receptors that are modulated by toxic substances are hormone receptors, particularly the ones belonging to the nuclear receptor family, whose activation can lead to undesired activities in the cells.

Endocrine-disrupting chemicals (EDCs) are commonly considered as compounds that mimic or block the transcriptional activities in the cells by binding to steroid hormone receptors. The definition of EDCs was later expanded to include those that act on the estrogen, androgen, and thyroid hormone receptors. The potential hazardous effects of EDCs on human health and environmental well-being are one of the global concerns, so modeling and predicting their toxicity is of the particular importance. In this work, we present the computational methods for modeling of hormone receptor-mediated toxicity, which could be useful for gaining an insight into the structural features of the chemicals responsible for activation or blocking of hormone receptors, as well as for prediction of the toxicity of new chemicals.

Key words: hormone receptor-mediated toxicity, endocrine-disrupting chemicals, toxicity modeling, toxicity prediction

## KN-6

**HYDROGEN-INDUCED PHENOMENA  
IN THIN FILMS OF METAL ALLOYS AND METAL SUPERLATTICES**

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Hydrogen and its isotopes can be dissolved spontaneously into many metals at ambient conditions, making them promising alternative, pollution free energy storage materials – issue that is extremely important in context of the looming energy crisis and approaching calamity of global warming. In addition, according to the latest investigations, the hydrogen incorporated into confined metals to nanosize geometries strongly influences their physical properties *i.e.* in broad term hydrogen could be viewed as a tuning agent of the properties of nanostructures making it an attractive research topic for that reason alone. Besides its applicative aspects, the hydrogen-induced phenomena are very interesting from fundamental point of view.

The interaction of thin films of  $\text{Fe}_{1-x}\text{V}_x$  ( $x = 0.5, 0.9$ ) and of superlattices, based on iron and vanadium monolayers with artificially introduced periodicity along the growth direction, with hydrogen gas under pressure between  $1\text{--}10^4$  Pa was studied by *in-situ* electrical resistivity measurements in a wide temperature range. The films were deposited using a magnetron sputtering technique under ultra-high vacuum conditions on  $10 \times 10 \times 0.5$  mm<sup>3</sup> polished single crystal MgO (001) substrates. The samples were deposited from targets of iron and vanadium onto the substrate held at 573 K and capped with palladium after cooling to room temperature in order to facilitate hydrogen loading and protect against oxidation.

At relatively low temperatures and low hydrogen concentrations, the residual resistivity of  $\text{V}_{0.9}\text{Fe}_{0.1}$  alloy increases with hydrogen pressure, following the modified Nordheim equation, which is similar to the behavior of pure vanadium thin film. In case of  $\text{V}_{0.5}\text{Fe}_{0.5}$  alloy, residual resistivity increases with hydrogen pressure but with a significant deviation from linearity. The experimental results indicate that hydrogen solubility is considerably reduced as the amount of iron in the alloy is increased. At higher temperatures, the residual resistivity unexpectedly decreases with increasing of hydrogen pressure right from the initial addition of hydrogen to the system. This behavior has not been reported before for thin hydrogen absorbing films. It is unusual since, under low pressure, it is expected that hydrogen absorption will be accompanied by occupation of interstitial sites within the metal (or alloy) crystal lattice generating scattering centers for the conduction electrons and consequently increasing the resistivity. This resistivity decrease in  $\text{Fe}_{1-x}\text{V}_x$  alloys becomes larger as the iron concentration in the alloy increases and with increasing temperature.

In order to explain the effect of dissolved hydrogen, *ab initio* calculations of the Fe-V system were performed and two ordered stable ground states were predicted, with compositions  $\text{Fe}_3\text{V}$  and  $\text{FeV}_3$ , in contrast to the empirical reports of a single intermetallic disordered  $\sigma$  phase. According to this, the observed reversible decrease of electrical resistivity with increasing of hydrogen pressure is experimental evidence of ordering in iron-vanadium alloys. Hydrogen induces structural changes acting as a catalyzing agent for phase separation due to the different affinities of vanadium (attractive) and iron (repulsive) towards hydrogen. In addition, the formation of ordered structures was confirmed by the kinetics of the resistivity changes upon variation of hydrogen pressure, where two stages can be distinguished: a fast and short initial part and a much slower subsequent process in which the resistivity changes direction, associated with hydrogen dissolution and phase transformation, respectively.

Keywords: hydrogen absorption, thin film, alloy, superlattices, ordering.

## KN-7

# THE ROLE OF QSAR IN CHARACTERIZATION OF NEWLY BIOACTIVE 1,2,4-TRIAZOLE COMPOUNDS, DRUG CANDIDATES

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The quantitative structure - activity relationship (QSAR) is a set of methods that tries to find a mathematical relationship between a set of descriptors of molecules and their activity. The descriptors: constitutional; topological; geometrical; electrostatic; quantum chemical; thermodynamic and molecular can be experimentally or computationally derived.

Drug design is an iterative process which begins with a compound that displays an interesting biological profile and ends with optimizing both the activity profile for the molecule and its chemical synthesis. The process is initiated when the chemist conceives a hypothesis which relates the chemical features of the molecule/s to the biological activity. Without a detailed understanding of the biochemical process responsible for activity, the hypothesis generally is refined by examining structural similarities and differences for active and inactive molecules. Compounds are selected for synthesis which maximizes the presence of functional groups or features believed to be responsible for activity.

Traditionally, the design of novel drugs has essentially been a trial-and-error process despite the tremendous efforts devoted to it by pharmaceutical and academic research groups. It is estimated that only one in 5,000 compounds investigated in preclinical discovery research ever emerges as a clinical lead, and that about one in 10 drug candidates in development ever gets through the costly process of clinical trials. Safe and effective drug candidates must have the appropriate pharmacokinetic characteristics in order to achieve and maintain effective concentrations at the site of action. Therefore, the modern process of discovering new drug does not focus only on the activity of compounds, but also on determination of the physico-chemical characteristics of the substance, a drug candidate and prediction of pharmacokinetic properties during the early stages of research. This approach, on one hand allows target synthesis of compounds that are expected to have relevant biological activity and favourable pharmacokinetic properties, and on the other hand when homologous series of structurally similar compounds is investigated, it defines the most promising compounds. Newly synthesized compounds have physico-chemical properties that will allow adequate absorption, distribution, metabolism and excretion (ADME properties).

The recent findings that 1,2,4-triazole nucleus is associated with diverse biological activities such as: analgesic, anti-asthmatic, diuretic, antihypertensive, antibacterial, antifungal and anti-inflammatory properties, prompt us to synthesized some new 1,2,4-triazole derivatives and to investigate their antibacterial and antifungal activities. Several article concerning the QSAR correlations between triazole activity and descriptors with different characteristic, has been published during the last years.

In the framework of this paper, application of QSAR method for biologically active 1,2,4-triazole compounds will be discussed and presented.

Keywords: QSAR, 1,2,4-triazole derivatives, descriptors, bioactive

## KN-8

### DISPERSION ANALYSIS

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Based on the dispersion relations of phonons and electronic excitations in crystals, dispersion analysis not only allows to determine the function of the complex dielectric tensor function in a certain spectral range and to reduce drastically the number of parameters to generate this function, but also facilitates the understanding of structure-properties relationships e.g. by connecting the outcome of quantum chemical calculations to experimental data.

The foundation of dispersion analysis reaches back to 1930 where it was first applied to analyze and understand the Reststrahlen band of crystals with cubic symmetry. The term itself was coined by Spitzer and Kleinman who were the first to investigate the reflectance spectra of optically uniaxial crystals by dispersion analysis in 1961. 17 years later efforts to analyze the reflectance spectra of monoclinic crystals succeeded. Shortly thereafter a first attempt was made to extend dispersion analysis to triclinic crystals.

Until recently, dispersion analysis could not be successfully applied to evaluate oscillator parameters of modes that have their transition moments perpendicular to the surface of an anisotropic crystal or a layered medium. The solution to this problem is to analyze simultaneously external and internal reflection spectra.

So far, spectra from the *a-c* plane of monoclinic crystals were analyzed under the assumption of normal incidence since the computational effort of applying a complete 4×4 matrix formalism for the calculation of the reflectance is comparably much larger. Recently we showed that considerable simplifications of this formalism are possible for the problem at hand. Therefore non-normal incidence can now be properly taken into account without significant increase in effort.

Triclinic crystals are characterized by a dielectric tensor function which cannot be diagonalized at the same time for both the real- and the imaginary part. This property distinguishes them from all other types of crystals where at least, as in the monoclinic case, a block diagonalization is possible. Recently, we were the first to succeed in carrying out a dispersion analysis on a triclinic crystal. The key to success is a scheme which involves the analysis of at least 9 reflection spectra in parallel.

Key words: Dispersion analysis, infrared reflectance spectroscopy, perpendicular modes, monoclinic crystals, triclinic crystals

## KN-9

# INFLUENCE OF MECHANICAL ACTIVATION ON THE PROPERTIES OF CERAMICS

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Mechanical activation of ceramics is a subject of interest for researchers mainly from the viewpoint of its practical use. The development of sustainable advanced material technologies is limited by the development of technologies for fabrication highly disperse powders, which control the powder activity (geometrical and structural) and contributes to synthesis of materials with particular properties.

The process of mechanical activation is based on mechanical impact on the treated system and a number of physical and chemical effects are initiated in it. The most effective and widely used method for generation of mechanical impact is grinding which is frequently implemented in planetary or vibro mill. Besides reduction of particle size and incensement of specific surface area during mechanical activation, a number of structural and electronic defects arise, ceramic materials become more chemically reactive but also phase transformations and chemical reactions can be performed.

Saving of electric power (due to lower reaction temperature and greater reaction speed) and synthesizing of novel advanced materials (which is difficult or impossible to be produced by other methods) as well as improving the properties of the end-ceramic products (such as mechanical, thermo physical, electrical, magnetic etc.) are the advantages of mechanical activation from the economic and technological viewpoint.

In our investigation mechanical activation was applied on the nano alumina as a sample of advanced ceramic material.

Keywords: mechanical activation, ceramics, nano alumina

**ANALYTICAL CHEMISTRY (A)**

**A-1**

**COMPARISON OF VARIOUS INJECTION MODES IN THE GC-MS  
ANALYSES OF HEXACHLOROCYCLOHEXANE ISOMERS**

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The analysis of hexachlorocyclohexanes, the most prominent of which is the gamma isomer lindane, is of continuing interest despite the fact that they have not been in use for many years, due to their slow degradation and persistence in the environment. It is of special concern in Skopje since it was produced in OHIS for only several years (from 1965 to 1972) and more than 30 000 tons of various isomers are deposited in dumps outside the plant. Some of these compounds leach in the soil and underground waters polluting the whole area.

Several modes of injection have been compared in order to develop a more suitable potential method for gas chromatographic trace analysis of these isomers in various matrices. These include the traditional hot splitless injection, but also hot pulsed splitless injection as well as cold splitless and solvent vent injections in a programmable temperature vaporizer (PTV). The first two modes have been tested on a gas chromatograph – mass spectrometer with a quadrupole analyzer (GC–qMS), while the last two on a two dimensional gas chromatograph with a time of flight analyzer (GC×GC–TOFMS). The initial results show that the pulsed splitless mode is superior to the splitless SIM mode for the GC–qMS, while the solvent vent is superior to all modes for the GC×GC–TOFMS giving improved signal-to-noise ratios compared to the other studied modes of injection.

Key words: hexachlorocyclohexanes, pulsed splitless injection, solvent vent injection, cold splitless injection, programmable temperature vaporizer

## A-2

# MICRO-RAMAN ANALYSIS OF TWO 17<sup>th</sup> CENTURY OLD-SLAVONIC MANUSCRIPTS

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Two manuscripts, *Struga Four Gospel* (17<sup>th</sup> century) and *Zrze Four Gospel* (16<sup>th</sup>/17<sup>th</sup> century) kept in the National and University Library "Sv. Kliment Ohridski" in Skopje, Republic of Macedonia, were analyzed in this study. They are written on paper in old-Slavonic language with old Cyrillic alphabet. In both books gospels begin with the ornament, followed by floral gilded letter.

Micro-Raman spectrometer LabRam 300 (Horiba Jobin-Yvon) equipped with a He-Ne laser (632.8 nm) operating with 6 mW at the sample was used for all *in situ* analyses. The obtained Raman spectra were compared to the reference database of pigments and their true nature was revealed except for green color, brown-purple ink and the gold. SEM-EDX was used as additional technique in analysis of the green and gold pigment as well as inks in both manuscripts.

*Ornaments*: *Zrze book* color palette consists of red, blue, brown and gold. The color palette in *Struga book* is richer compared to *Zrze book*, with additional green and yellow color. The blue color in ornaments in both books is identified as a mixture of azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ) and indigo ( $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$ ), gold was used for gilding, while gall ink for framing. Yellow pigment used in *Struga book* was orpiment ( $\text{As}_2\text{S}_3$ ) while green pigment was identified as organo-Cu complex. Some differences were observed in the use of the red pigment; in *Struga book* only vermilion ( $\text{HgS}$ ) was used to achieve the red color, while in *Zrze book*, a mixture of vermilion and red lead ( $\text{Pb}_3\text{O}_4$ ) was used. The presence of pure gold in gold pigments applied for gilding in both books was confirmed using SEM-EDX.

*Inks*: The text in *Zrze book* is written in four colored inks: black-brown, blue, red and brown-purple, while in *Struga book* the inks are black-brown, blue and red. Gall ink was identified as black-brown ink in both books, while mixture of azurite and indigo was used as blue ink. In *Struga book* vermilion was used as red ink, while in *Zrze book* the mixture of vermilion and red lead was used. The fourth ink in *Zrze book*, the brown-purple one, did not provide Raman spectrum and its identification is still under consideration.

Keywords: micro-Raman spectroscopy, manuscripts, pigments, inks.

### A-3

## MICRO-RAMAN PIGMENT ANALYSIS OF THREE ICONS FROM REPUBLIC OF MACEDONIA

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As a part of our study of pigments in medieval frescos and icons in Republic of Macedonia, three icons, from three different periods were analyzed: “Hvalite Gospoda” from Kučevište monastery, village of Kučevište (beginning of 17<sup>th</sup> century), “Bogorodica so Isus Hristos” from Karpinski monastery, village of Orah (16<sup>th</sup> century) and “Sv. Vasilie and Sv. Nikola” from Gallery of icons in Ohrid (11<sup>th</sup> century).

Analyses were performed on small paint chips provided by restorations/conservators, using micro-Raman spectrometer LabRam 300 (Horiba Jobin-Yvon) equipped with a He-Ne laser (632.8 nm) with 6 mW at the sample. For identification of the goid paint, SEM-EDX was applied.

Micro-Raman spectroscopy was applied in characterization of the pigments and grounds. All icons are painted on ground surface, which mainly consists of calcite, although in “Sv. Vasilie and Sv. Nikola” gypsum was found in the ground as well. The color palette in all three icons was similar with white, beige, gold, red and blue paint. The identified pigments (lead white, calcite, goethite, lepidocrocite, orpiment, hematite, vermilion, red lead, indigo, lazurite, magnetite and carbon black) are traditional, mineral based and known since antiquity. Brown and beige colors were obtained using different amount of several pigments: white, yellow, red and black. The most interesting result was identification of additional yellow pigment - lead tin yellow type II in “Sv. Vasilie and Sv. Nikola” (11<sup>th</sup> century). This pigment is widely used in the medieval icons in Western Europe starting from the 14<sup>th</sup> century, but it was not identified prior to 1300 A.D. Thus, the identification of this pigment in 11<sup>th</sup> century icon could be interpreted in several ways: (a) the use of this pigment in Byzantine countries started earlier than in Western Europe; (b) the icon has been repaired/refreshed in the later period or (c) the dating of the icon is not correct.

Keywords: micro-Raman spectroscopy, icons, pigments.

**A-4**

**A NOVEL CATALYTIC SPECTROPHOTOMETRIC DETERMINATION OF  
YTTRIUM (III)**

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A novel highly sensitive, inexpensive and accurate method for determination of ultra micro quantities of Y(III) has been developed. The reaction between 4-hydroxycoumarin and permanganate ion in acetate buffer, catalyzed by Y(III), was applied as the indicator reaction. The reaction was followed spectrophotometrically by measuring the decrease in absorbance at 525 nm as a function of time. The important variables that affected the reaction rate were investigated and the optimum conditions giving maximum sensitivity were established. The sensitivity of the method is 20 ng/cm<sup>3</sup> for the concentration range of Y(III) from 2x10<sup>-8</sup> to 2.25x10<sup>-7</sup> g/cm<sup>3</sup>. The kinetic equations were established on three different temperatures and rate constants were calculated. The accuracy and precision were validated statistically and the probable relative error ranges from 1.00-6.00 % for Y(III) concentrations from 20-500 ng/cm<sup>3</sup>. The influence of various interferents on the proposed determination was examined and the possibility of its analytical application based on synthetic samples was evaluated.

Keywords : Catalytic spectrophotometric Y(III) determination, reaction rate method

**A-5****IMPLEMENTING FTIR-ATR TECHNIQUE TO DETERMINE STABILITY OF THE PROBIOTIC *LACTOBACILLUS CASEI* LOADED IN WHEY PROTEIN-Ca-ALGINATE MICROPARTICLES**

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Fourier transform infrared spectroscopy (FTIR) is widely used to study the molecular structure of various compounds, but also for rapid identification of microorganisms, especially probiotics. The aim of this study was to determine the stability of the probiotic *Lactobacillus casei* during incorporation in microparticles comprised of Ca-alginate and whey proteins aimed to protect the probiotic during application in food/pharmaceutical products, storage and *in vivo* administration. FTIR-ATR spectra were recorded at room and at temperatures needed for the vitality of the bacteria. The spectra were recorded using Golden Gate™ ATR attachment, in frequency range of 4000-400 cm<sup>-1</sup>. Spectra of non-encapsulated *Lactobacillus casei* and released from the microparticles were compared.

The spectra obtained from the released *Lactobacillus casei* showed almost identical features with non-encapsulated specimen, including the band at 1127 cm<sup>-1</sup> from the lactic acid obtained as fermentation product. Because of the complex structure of the investigated sample, a rough assignment of the corrected FTIR-ATR spectra has been made. The bands at ~2845 cm<sup>-1</sup> and ~2929 cm<sup>-1</sup> due to asymmetric stretching and at ~1372 cm<sup>-1</sup> and ~1430 cm<sup>-1</sup> due to deformation vibrations of -CH<sub>3</sub> and CH<sub>2</sub>- were detected. A band at ~1730 cm<sup>-1</sup> due to the C=O stretching vibration of the ester groups into the fatty acids and lipids together with Amide I and Amide II bands at ~1620 cm<sup>-1</sup> and 1530 cm<sup>-1</sup> from proteins were also observed. In the IR fingerprint region, the symmetric and asymmetric stretching from the phosphoric acid in nucleic acids at 1030 cm<sup>-1</sup> and 1190 cm<sup>-1</sup> was found, together with the C-O-C deformation vibration from the polysaccharides (900-1200 cm<sup>-1</sup>) bonded to the glycopeptides and lipopolysaccharides of the cell wall.

In conclusion, according to the FTIR-spectroscopic studies, the stability of the probiotic cells during microencapsulation was preserved.

Keywords: FTIR, *Lactobacillus casei*, microparticles.

**A-6**

**RAPID DETERMINATION OF TOTAL CYANIDE IN SOILS BY  
HEADSPACE GAS CHROMATOGRAPHY**

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Cyanide compounds in the environment originate mainly from a variety of industrial sources. Since cyanide compounds can release the extremely toxic free cyanides (hydrogen cyanide, HCN, and cyanide ion, CN<sup>-</sup>), there is a need for rapid and precise determination of cyanides in air, waste waters, ground waters, and soils. This study was conducted to determine whether a headspace gas chromatography, can be used for analyzing total cyanide in heterogeneously contaminated soil samples. The samples represent a wide range in cyanide concentrations, from 1 to 1000 mg kg<sup>-1</sup> CN<sup>-</sup>. Sample preparation was restricted to air-drying and sieving.

Gas chromatographic analysis was carried out with a GC equipped with a flame ionization detector (FID) and a Elite 624 capillary column (30 m x 0.53 mm i.d., 1 µm film thickness). The column temperature was programmed from 60°C (1 min hold) to 130°C (2 min hold) at 30°C/min. Total GC run time was 6 min. HCN is liberated during an incubation step for 10 min at 70°C by 2.0 M hydrochloric acid from the matrix in a headspace vial. This method is simple, rapid, and specific for cyanide and does not suffer from any interference. The LOD was 0.2 mg CN<sup>-</sup>/ kg and the calibration curve was linear from 4.0 to 300 mg CN<sup>-</sup>/ kg (r<sup>2</sup>=0.9991). The within-run coefficient of variation in this range was 8% or less. Using laboratory prepared samples with known amounts of cyanide, recoveries greater than 95% could be established. This proposed method was efficient and simple and can be used for an accurate analysis of total cyanide in soil samples.

Keywords: GC determination; total cyanide; soil; headspace gas chromatography

## A-7

### DETERMINATION OF CALCIUM PROPIONATE IN BAKERY PRODUCTS

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The propionic acid in form of calcium propionate indexed in the U.S. Food and Drug Administration's GRAS list is commonly applied antimicrobial agent in bakery products. In the Republic of Macedonia, the maximum values for the presence of propionate in bakery products are prescribed in the Rulebook on additives.

The need for determination of calcium propionate quantity in bakery products present on the market has set the aim to develop a simple, accurate and reproducible method. For that purpose, headspace gas chromatography was developed. Gas chromatography analysis was carried out with a GC equipped with a flame ionization detector (FID) and a DB-WAX capillary column (30 m x 0.53 mm i.d., 1 µm film thickness). The initial oven temperature of 110 °C (1 min hold) was programmed to 190 °C final temperature (0.5 min hold) at 30 °C/min rate. The samples of calcium propionate used as standard and samples of bakery products were prepared in deionized water with pH = 3.0. The calibration curve in the range of 0.1-1 mg/mL was linear ( $r^2 = 0.9916$ ). The recoveries greater than 95% were established in the bakery products prepared in laboratory conditions. The method proposed for control and determination of potassium propionate in samples of bakery products was rapid, efficient and simple with no prior preparation or solvent extraction of calcium propionate.

Keywords: bakery products, calcium propionate, headspace gas chromatography

**A-8**

**SPECTROPHOTOMETRIC METHOD OF IODINE DETERMINATION IN  
FOOD GRADE SALT**

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Iodine is an essential trace element in human nutrition. It is a vital part of the thyroid hormones that play an important role in the development of brain function and cell growth. Iodine deficiency reduces the production of thyroid hormones in humans and animals, leading to morphological and functional changes of the thyroid gland and reduction of the formation of thyroxin.

One of the methods for the protection from iodine deficiency is the iodization of the salt for human consumption. In the Republic of Macedonia, the iodization of the food salt is compulsory. In accordance to the Rulebook for food salt quality, iodine concentrations of 20-30 mg in kg food salt provided by adding of potassium iodate are prescribed.

The commonly used routine method for determination of iodine in food products including food grade salt is titrimetric method with sodium thiosulphate. Considering the shortcomings of this analytical procedure associated with low accuracy and reproducibility imposed the need and aim to develop a simple and accurate method for iodine quantification in food salt.

The iodine dissolution in chloroform and its quantity determination by the absorbance reading of the colour of the formed chloroform-iodine complex was the initial idea of developed a spectrophotometric method for iodine quantification. The characteristic of iodine equivalent to iodate in acid medium to release from the iodide and as elemental to dissolve in chloroform was used. The relation between the intensity of the colour on the chloroform-iodine complex with the iodine concentrations was linear over a range from 0.01 to 0.1 mg/mL ( $r^2=0.9977$ ). The detection and quantification limits were found to be 0.005 and 0.01 mg iodine/mL. The obtained results demonstrated that the procedure is accurate, precise and reproducible (relative standard deviation < 3 %) and can be applied for iodine determination in food grade salt samples iodized with potassium iodate.

Keywords: iodine quantification, food grade salt, chloroform-iodine complex, accuracy, precision

## A-9

# DEVELOPMENT OF A SIMPLE VOLTAMMETRIC METHOD FOR DETERMINATION OF ANTIOXIDANT CAPACITY OF VEGETABLE OILS

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Oxidative stress comprises a series of processes in which an excess of reactive oxygen species (ROS) are generated in living cells. Owing to their strong oxidizing activity, free radicals can damage most of the physiologically active molecules and increase the risk for many serious pathologies, such as asthma, atherosclerosis, cardiovascular disease, diabetes, cancer, Alzheimer's and Parkinson's disease. Vegetable oils possess a high resistance to the oxidative degradation due to the presence of polyunsaturated fatty acids and significant amounts of antioxidative phenolic compounds. In this study we present a new, rapid and simple voltammetric method for determination of total antioxidant capacity of vegetable oils. The antioxidant capacity of vegetable oils has been estimated by measuring the rate of homogeneous redox reaction with  $\text{ABTS}^{\bullet+}$  radical cation (2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid)) by means of cyclic voltammetry.  $\text{ABTS}^{\bullet+}$  radical cation was electrochemically *in situ* generated at the surface of glassy carbon electrode by electrochemical oxidation of ABTS in ethanol electrolyte solution. Thus, the  $\text{ABTS}^{\bullet+}$  radical cation serves as a redox mediator for catalytic oxidation of antioxidants present in studied vegetable oils.

Keywords : antioxidant capacity, vegetable oils, cyclic voltammetry, ABTS.

**A-10**

**COMPARISON OF DIFFERENT EXTRACTION MIXTURES FOR  
CHARACTERIZATION OF POLYPHENOLIC COMPOUNDS IN  
RASPBERRIES USING HPLC-DAD-ESI-MS<sup>n</sup> AND UV-  
SPECTROPHOTOMETRY**

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Raspberry fruits (*Rubus idaeus*) are known as good source of antioxidant phytochemicals with demonstrated activity in the prevention of chronic diseases. These berry fruits as rich sources of health promoting compounds can be also used as a raw material or additives in production of dietary supplements, food, drinks etc.

Six different solvent mixtures containing acetone or methanol pure or combined with water and acetic acid were tested for their efficiency for extraction of phenolic compounds from *Rubus idaeus* (var. *Willamete*) belonging to the five groups of polyphenols: anthocyanins, flavonols, flavan-3-ols, hydroxycinnamic acid derivatives and conjugated forms of ellagic acid. Twenty five compounds from these five groups have been separated using HPLC and identified by their UV-spectra and tandem mass spectra (MS<sup>n</sup>) with electrospray ionization. Sanguin H-10 and sanguin H-6 were found as major ellagitannins and cyanidin-3-sophoroside and cyanidin-3-glucoside were the most abundant anthocyanins in all extracts.

The extraction yield with regards to the extraction solvent composition was evaluated by measurement of total phenolic compounds and total anthocyanins using spectrophotometric methods. The total polyphenols content in the various extracts was in the range from 732.8 g/kg to 1726.1 g/kg expressed as gallic acid. Total anthocyanins content obtained with the pH-differential method was in the range between 133.3 to 176.8 g/kg expressed as cyanidin 3-glucoside. The extraction with pure acetone gave the best results for the qualitative and quantitative assay of the polyphenols present in raspberries since all 25 compounds were detected only in these extracts in quantities higher or comparable to the other extraction solvents tested.

Keywords: raspberry, *Rubus idaeus*, polyphenols, HPLC, MS

## A-11

### APPLICATION OF MICRO-RAMAN AND INFRARED SPECTROSCOPY FOR THE ANALYSIS OF EXPLOSIVES

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Micro-Raman and infrared spectroscopy were used for detection and identification of nine explosives from the collection of the Forensic Department in Ministry of Interior – Skopje (seized in the period between 2001 and 2011), as well as two explosive substances and residues after explosion (post-blast).

In order to compare the efficiency of the Raman data, two micro-Raman spectrometers with different resolutions and spectral ranges were used: (a) FORAM 685-2, (at the Forensic Department, Ministry of Interior in Skopje) and (b) Horiba Jobin-Yvon LabRam-300 (at the Institute of Chemistry, Faculty of Natural Sciences & Mathematics). As expected, the Raman data recorded with the later one, gave much better results. The infrared spectra were recorded with FT-IR 100 Perkin Elmer interferometer (at the Forensic Department, Ministry of Interior in Skopje).

The obtained infrared, and in particular the micro-Raman spectra provided efficient and quick results for the detection of TNT (2,4,6-trinitrotoluene); PETN (pentaerythritol tetranitrate), powder and plastic; RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) powder and plastic; picric acid, amonex; dynamite and lazarit C-2. These results were then compared with the third technique, gas chromatography coupled to mass spectrometry, frequently used in the past for detection of the explosives in post-blast explosions.

Due to the non-destructive character of micro-Raman spectroscopy, as well as its efficiency, all explosives, except dynamite, were easily identified. Infrared spectroscopy gave good results when one component explosives are analyzed, while in the case of mixtures it is less efficient. The results obtained by the technique of gas chromatography coupled to mass spectrometry were satisfying, but, the investigations showed that without appropriate column, certain conditions and pretreatment of each sample, definite results can not be obtained.

An attempt was made to identify explosives and traces of explosives (post-blast) *in situ*. For this, tablets prepared from soil collected from two locations (the crater and the path of detonating cord) were prepared and scanned over a certain area using automatic XY mapping stage. However, except for the main components of the soil (such as quartz, carbonates, iron oxides and aluminosilicates) no other traces of explosives were identified. The most appropriate method for identification of traces of explosives in post-blast explosions is already well defined method for acetone solutes and analyzing the obtained extract by Raman or infrared spectroscopy.

Keywords: explosives, residues after explosion (post-blast), micro-Raman and infrared spectroscopy, Gas chromatography coupled to mass spectrometry

**A-12**

**ASSAY OF CANNABINOIDS IN *Cannabis sativa* L. FROM MACEDONIA  
USING GAS CHROMATOGRAPHY COUPLED TO MASS  
SPECTROMETRY**

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The work presented in this thesis involves validation of an analytical method for identification and quantification of cannabinoids in plant samples of *Cannabis sativa* L. as well as in its products *i.e.* opiates as marihuana, hashish etc. using gas chromatography coupled to mass spectrometry. Analysis was performed for characterization of the three most abundant cannabinoids: cannabidiol (CBD), tetrahydrocannabinol (THC) and cannabinol (CBN) in 43 samples of *Cannabis sativa* L. seized by the Ministry of Interior in the period from 2008 to 2010 in 12 cities in the Republic of Macedonia. These samples were assayed in order to study the content and patterns of cannabinoids in *Cannabis sativa* L. from our climate.

A series of examinations were made for optimization of the conditions for obtaining satisfactory separation and shape of the chromatographic peaks followed by method validation by checking its accuracy, reproducibility, linearity, limit of detection and quantitation. Adequate validation data gave support to application of this method for routine analyses of the three cannabinoids in forensic laboratories.

Quantification of CBD, THC and CBN was then performed in the examined plants and the obtained results for the average cannabinoids content was: 0,957 % for CBD; 1,126 % for THC and 0,062 % for CBN. Principal component analysis was used for statistical treatment of the results in order to examine if there is regional grouping of the samples, but no such grouping was detected, which was attributed to the non-systematic collection of the material, variable growing conditions and seed origin. The obtained results were also compared to the one for the cannabinoids content in other regions of the world and similar contents were found with samples from Greece, Denmark, Granada, Antigua etc. (for THC), Germany, Poland, France, Hungary etc.(for CBD).

**Keywords:** *Cannabis sativa* L.; cannabinoids; tetrahydrocannabinol; cannabinol; cannabidiol; GC-MS

**A-13**

**FAST SIMPLE CHROMATOGRAPHIC METHOD FOR ENALAPRIL  
QUANTIFICATION IN PHARMACEUTICAL DOSAGE FORM IN THE  
PRESENCE OF CHAOTROPIC PERCHLORATE ANION IN THE ELUENT**

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The ACE-inhibitor Enalapril is one of the attention needed API in its quantification chromatographic method, in its pharmaceutical dosage forms and in the other matrices. It is almost always followed with employment of high temperatures, and low and acidic inorganic constituents of mobile phase, which is in majority cases harmful to the HPLC column matrix. The peak shapes irregularities, fronting, leading with high asymmetry factor, abnormal chromatographic behavior in injected mass and volume, flow rate, are caused by its proline-like based chemical structure. There are many published and described HPLC method for Enalapril quantification, but we concepted, designed and developed one of the simplest possible method, by using regulated concentration of perchlorate anion in mobile phase and obtained perfect peak symmetry and promising separation power for the most frequent related compounds, Enalaprilate and Diketopiperazine, which are very different in their polarity and hydrophobicity in acidic medium, resulting in the first and last their position on the chromatogram. Many different vendors of L7 column (RP C8-octylsilane silica based) can be used without significant changes in chromatographic quality parameters. We found that use of Merck's RP Select B columns are one of the most applicable, in the dimensions of 75, 125 and 250 x 4 mm with 5 µm particles, depending on the target of the assay.

Keywords : HPLC, Reversed phase, UV, Enalapril, chaotropics

**A-14**

**DEVELOPMENT OF FAST AND SIMPLE HPLC METHOD FOR  
SIMULTANEOUS QUANTIFICATION OF HYDROCHLOROTHIAZIDE  
AND ENALAPRIL IN SOLID DOSAGE PHARMACEUTICAL FORM**

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Combination of the active pharmaceutical ingredients Enalapril and Hydrochlorothiazide in one single solid pharmaceutical dosage form is very common in the pharmaceutical products menu. These chemical entities are very different in their chemical properties, based on their chemical structures, and these facts are dictating the development of their chromatographic quantification methods. Even Pharmacopoeia's described methods for their quantification assays are in separate chromatographic methods. This prompted us to design and develop a simultaneous chromatographic method for quantification of these pharmaceuticals. This was accomplished with RP HPLC method using Supelco-LC-8 DB 150 x 4 mm, 5  $\mu$ m column. The successful and satisfying separation was achieved with acidic buffer at pH=2.3 in combination with acetonitrile at 50 °C, 1 ml/min flow rate and 210 nm UV monitoring and 10  $\mu$ l injection volumes. Full attention was dedicated to sample preparation solvent which strongly governs the peak shapes and their resolution. Five different RP column vendors with L7 and L1 categories were tested, and the best method can separate Hydrochlorothiazide and Enalapril with tR about 1.6 and 2.3 minutes respectively, in less than 3 minutes and with resolutions higher than 2.3 and 4, and with very good peak symmetries, about 1.2 and 0.85 respectively. The method allows for re-optimisation possibly caused for technological constituents and sensitivity.

Keywords : HPLC, Reversed Phase, Hydrochlorothiazide, Enalapril, UV

A-15

**WIDE PORE PREFERRED IN DEVELOPMENT AND VALIDATION OF  
HPLC METHOD FOR QUANTIFICATION OF NIMESULIDE AND TWO  
PARABENS IN SEMISOLID PHARMACEUTICAL DOSAGE FORM  
VENTOR GEL 2%**

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The aim of this work is development of RP HPLC method for simultaneous quantification of the NSAID Nimesulide and two paraben-based preservatives Nipagin and Nipasol in our semisolid pharmaceutical dosage form 2% Venter gel. The method was tested with many L1 columns and the best results were obtained with Discovery C18 150 x 4,6 mm, 5µm particles, equilibrated with approximately equal volumes of methanol and 50mM phosphate buffer at pH=6, at UV monitoring at 254nm, at 30 °C, and flow rate 1 ml/min by injection of 10µl sample. These chromatographic conditions produced perfect system suitability parameters and validation performance statistics governing selectivity, accuracy, recovery, reproducibility and ruggedness. The RSD linear regression calculation of Nimesulide was  $Y = 0.9860x + 0.0029$  which showed  $R^2 > 0.999$  for all three quantifying components, with excellent peak symmetries and high resolutions with parabens, which enables further improvement in runtime method, limits of quantification and detection. The wide pore columns of L1 category showed better preferring characteristics for better system suitability performances. Nimesulide is molecule that requires more attention in extracting procedures and precautions in selecting pH value of mobile phase. In our research working with buffers within the cited pKa region 5.8-6.4, showed to be beneficial in fine tuning of peak retention and not to exert peak skewing or splicing. The method is easy for redesign depending of purpose, routine analysis or stability study.

Keywords : Nimesulide, HPLC, UV, Reversed phase.

## A-16

# ELECTROSPRAY IONISATION STUDY OF PROTEINS. ESI-MS SPECTRA OF CASEIN AND BETA LACTOGLOBULIN

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The techniques of electrospray/ionization (ESI) and matrix-assisted laser desorption/ionization (MALDI) have revolutionized biological mass spectrometry (MS). Significant amount of data can be derived from mass spectra of biological samples such as peptides and proteins and DNA. Besides the determination of the molecular mass of a given compound and the identification of proteins by accurate mass determination of their proteolytic fragments, MS is capable of providing structural information (*i.e.*, sequences) for peptides. Electrospray ionization is contributing to the formation of singly charged small molecules but is also well known for generating multiply charged species of larger molecules. This is an important process because the mass spectrometer measures the  $m/z$  and, therefore, multiple charging makes it possible to observe very large molecules with an instrument having a relatively small mass range. Fortunately, software available with all electrospray mass spectrometers facilitates the molecular mass calculations necessary to determine the mass of the multiply charged species.

Casein and beta lactoglobulin raw ESI mass spectra were collected with Agilent 6330 ion trap instrument in the 50/50 H<sub>2</sub>O/TFA mixture. Both positive and negative-ion spectra are obtained. For positive-ion mode, 0.1% trifluoroacetic acid (TFA) was usually added into the analyte solution to enhance protonation and increase sensitivity. The most obvious features in the casein and beta lactoglobulin ESI MS spectra were series of peaks from the ions with multiple charge states from +10 to +22 in the 800 to 2300  $m/z$  range. Standard open source and Agilent software in the process of data collection and processing was used.

Keywords: electrospray/ionization (ESI), ESI MS spectra, casein, beta lactoglobulin

**A-17**

**ELECTROSPRAY IONISATION STUDY OF SMALL PEPTIDES. ESI MS<sup>n</sup>  
SPECTRA OF L-LEUCYL-GLYCINE**

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ESI mass spectra of the L-leucyl-glycine were collected with Agilent 6330 ion trap instrument in the both positive and negative-ion mode. The most obvious features in ESI MS spectra are intensive peak of the molecular ion of the studied compound L-leucyl-glycine at 189  $m/z$  value.

However in the ESI MS<sup>1</sup> spectrum, several other peaks at 174, 211, 234 and 273  $m/z$  values, were also observed. These peaks are probably due to defragmentation of the methyl group from the leucyl residues on the C-terminal isopropyl group in the dipeptide and other defragmentation and addition processes. The peaks at 174 and 160  $m/z$  values are due to defragmentation of the first and second terminal isopropyl residue methyl groups.

In addition, MS<sup>2</sup> and MS<sup>3</sup> experiments were started. Some mass spectral features are observed which are consistent with structure-specific fragmentation reactions for different y and b- types fragments. The spectra are in agreement with the work of Harrison *et al.*, (*Structure and Fragmentation of b<sub>2</sub> Ions in Peptide Mass Spectra*, J. Am. Soc. Mass. Spectrom. 2000, 11, 427–436).

Careful guided MS<sup>2</sup> and MS<sup>3</sup> experiment together with theoretical *ab initio* calculations are necessary to estimate the thermodynamically ions stability in the ionization process of the different fragments for assignments of the observed peaks observed at 161, 172, 189, 206 in MS<sup>2</sup> and 190 and 207  $m/z$  values in MS<sup>3</sup> spectra.

Keywords: ESI MS spectra, L-leucyl-glycine, molecular ion, MS<sup>2</sup> and MS<sup>3</sup> spectra

## A-18

### MASS SPECTROMETRIC IMMUNOASSAY ANALYSIS OF PROTEINS

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Mass spectrometry is an analytical technique for protein research and for the study of biomolecules in general. Driven by the need to identify, characterize and quantify proteins with increasing sensitivity and from complex samples, a wide range of new mass spectrometry-based analytical platforms and experimental strategies have emerged. In this work we utilized mass spectrometry instrumentation in the context of current and emerging research strategies in protein science, for screening and evaluation of biomarkers in plasma in high throughput mode, and with high selectivity and sensitivity.

Analysis of human serum samples was done by matrix-assisted laser desorption/ionization mass spectrometry (MALDI MS) in order to detect proteins or protein fragments of unknown identity, which can be used as potential biomarkers for early detection of diseases an/or their treatment.

For quantification, internal reference standard was incorporated into the analyses, and its mass and intensity were utilized to normalize the signals from the targeted proteins. The results obtained for the human plasma protein leptin demonstrate highly-sensitive, reproducible, and fast quantification using mass spectrometry as a method of detection.

Key words: human serum; biomarkers; mass spectrometry; leptin; proteomics (protein fragments)



## A-20

# ANALYSES OF BALL POINT INKS, GELL PEN INKS AND MARKERS USING MICRO-RAMAN AND FT-IR SPECTROSCOPY

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Micro-Raman and FT-IR spectroscopy were applied for identification of inks, solvents and/or fillers in green and blue ball point inks, gel pen inks and markers. Six different ball point inks (Bic, Office Point, Paper mate, Beifa, Pensan and Ai Hiao), five gell pen inks (Beifa, Uniball, Paper mate, Schneider and Pelikan) and four different markers (Vidal, Bic, Grasp and Schneider) were taken for this analysis.

The Raman spectra were recorded for all type of inks by deposition directly on the paper while the FT-IR spectra were recorded from a spot of inks dissolved and pressed in KBr pellets.

The resulting Raman spectra are of good quality enabling identification of practically all pigments used in blue and green inks. Comparison with the spectral ID database of referent Raman spectra showed that most of the blue and green inks belong to halogenated and/or sulfonated derivatives of metal (M) phtalocyanine group of complex compounds. In those compounds, the metal is usually copper, but it can vary from Zn though Fe, Co and Ni. For most of the blue and green pigments, the coordination metal was estimated using the most intensive Raman band due to the breathing of the phtalocyanine ring, appearing between 1500 and 1550  $\text{cm}^{-1}$ . It was reported in literature that this band decreases in frequency with the change of the metal in a phtalocyanine complexes as follows:  $\text{Zn} < \text{Cu} < \text{Fe} < \text{Co} < \text{Ni}$  [1]. According to this, for the green pigments in the ball point and gel pen inks, it was estimated that the metal in phtalocyanine complexes is either Cu or Fe, while for the most of the blue pigments the coordination metal is iron.

All recorded IR spectra of the green ball point inks, gel pen inks and markers are similar with each other indicating the presence/dominance of the same and/or similar solvent/fillers.

The solvent (filler) from the gel pen inks was isolated and its Raman and IR spectrum was recorded. On the basis of its spectra, the solvent was identified as hexanol while the filler was most probably a resin.

Keywords: Raman spectroscopy, FT-IR spectroscopy, Ballpoint pen ink, Gel pen ink, Marker

**A-21**

**SPECTROPHOTOMETRIC DETERMINATION OF SULFADIMIDINE AND SULFAMURAZOLE IN VETERINARIAN MEDICINAL PREPARATIONS**

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Quality control of veterinary medical product is particularly important for assuring proper and effective drug administration resulting in presence of safe levels of residues in food of animal origin. In clinical practice sulfonamides that have been administered individually or in mixtures include sulfadiazine, sulfadimidine, sulfamethoxazole and trimethoprim which increases the activity of sulfonamide.

A simple, rapid accurate and economically acceptable spectrophotometric method for the determination of sulfonamides on veterinarian drugs has been developed. Analyzes were performed on Varian Carry 50 UV/Visible spectrophotometer, in a 1-cm cell at wavelength range from 190 to 350 nm, with resolution 0.5 nm and scan rate of 300 nm/min. Water was used as solvent, because of its availability it is more ecological and cheaper solvent.

The methods have good linearity in the concentration 0.8–40 µg/ml for sulfadimidine and 0.8–30 µg/ml for sulfamurazole. The calibration curves demonstrated correlation coefficients greater than 0.9993 and 0.9989, respectively. The LOD of 1.28 µg/ml (sulfadimidine), 1.80 µg/ml (sulfamurazole) and LOQ of 4.25 µg/ml (sulfadimidine) and 6.00 µg/ml (sulfamurazole) respectively, were calculated. Optimization was performed by selecting filters and the accuracy of the method was confirmed via standard addition method, where the mean recoveries were 101.4% and 90.6% for sulfadimidine and sulfamurazole respectively.

The developed method was applied for determination of sulfadimidine and sulfamurazole in veterinarian drugs Sulfadimidine, Neosulfox (multicomponent drugs which contains sulfadimidine, oxytetracycline and neomycine) and Trimetosul.

Keywords: veterinarian drugs, sulfadimidine, sulfamurazole, UV spectrophotometry

A-22

## **SPECTROPHOTOMETRIC DETERMINATION OF SULFAMETHOXAZOLE AND TRIMETHOPRIME IN PHARMACEUTICAL PRODUCT**

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Sulfamethoxazole (SMX) and trimethoprim (TMP), frequently combined in chemotherapeutic practice, are analysed by a variety of chromatographic and conventional methods. In clinical practice sulfonamides that have been administered individually or in mixtures include Co-trimoxazole, Bactrim, Bactrimol among others. In this investigation, a spectrophotometric method was employed with a Varian Carry 50 UV/Visible spectrophotometer.

Extraction with several mediums such as acetonitrile, ethanol, methanol and water, was tested. Ethanol was chosen as solvent because it is a good solvent for spectrophotometry and it completely dissolves the sample. The sulfamethoxazole shows  $\lambda_{\max}$  at 271 nm and the linearity plot yielded a correlation coefficient of 0.997. The method has good linearity in the concentration 0.8–30  $\mu\text{g/ml}$ . The LOD of 1.72  $\mu\text{g/ml}$  (SMX), and LOQ of 5.74  $\mu\text{g/ml}$  (SMX) were calculated. The accuracy of the method was confirmed via standard addition method, where the mean recovery was 100.33% for SMX. The method was successfully applied for the analysis of SMX in the human drugs Co-trimoxazole, Bactrim and Bactimol.

Using the developed procedure, it was possible to analyze only SMX in pharmaceutical preparations without separating it from the excipients. Direct calibration method was not applied to TMP, because the absorbance of TMP at 284 nm was overlapping with the absorbance at higher wavelength of SMX.

This problem was solved through predetermined system of equations based on molar absorption coefficients of SMX and TMP, which was tested on the binary systems for SMX and TMP in aqueous solutions.

Keywords: pharmaceutical, sulfamethoxazole, trimethoprim, UV spectrophotometry

## A-23

### DETERMINATION OF SELENIUM IN FOOD SUPPLEMENTS BY USING SPECTROPHOTOMETRIC METHOD

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A simple and low cost spectrophotometric method is optimized for selenium determination in Food Supplements. Variation of single parameter method was used for the optimization of the method of analysis. The methodology is based on the reaction of selenium with iodide ions in acid medium in the presence of amides. Free iodine is released in solution, which reacts with amides by giving a violet color in sample solution. The measurements were performed at  $\lambda_{\max} = 574 \text{ nm}$  ( $\epsilon_{\max} = 144660 \text{ A} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) in 1 cm glass cell. The performance, sensitivity and accuracy of this method is very high. To avoid the interferences of the matrix in the determination of selenium the standard addition method was used which had a high performance and a linear calibration graph with a very good linear coefficient  $R^2 = 0.9996$ .

The Food Supplement samples (2 different food supplements) were chosen occasionally in different pharmacies in Tirana (5 samples for each food supplement). The selenium concentration per tablet ranged from  $25.38 \pm 1.47 \text{ } \mu\text{g}/\text{tablet}$  and  $54.86 \pm 1.36 \text{ } \mu\text{g}/\text{tablet}$  by using standard addition method.

The selenium concentration determined in the analyzed samples is within the range of the concentration declared in the patient information leaflet for both food supplements analyzed ( $25 \text{ } \mu\text{g}/\text{tablet}$  and  $55 \text{ } \mu\text{g}/\text{tablet}$ ) of the pharmaceutical companies for these food supplements.

The accuracy of the analysis was checked by recovery of the spikes which was in the range of 97-102%. The method yielded reproducible results with  $\text{RSD} < 4.66\%$ .

Keywords: spectrophotometry, Food Supplement, Selenium concentration, calibration graph, coefficient of linearity

**A-24**

**SAMPLE PREPARATION FOR THE DETERMINATION OF  
ARSENOLIPIDS WITH GC-MS IN FISH OIL**

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Arsenic occurs naturally in many types of seafood as water-soluble and lipid-soluble organoarsenic compounds. Water-soluble compounds have been well characterized; lipid-soluble arsenic species, although found in about 50 years ago have been rarely investigated. During the last years several new arsenolipids were identified in marine samples which are categorized in three classes: arsenic-containing fatty acids, arsenic-containing hydrocarbons, and arsenic containing sugarphospholipids. Quantification of these compounds with HPLC-ICPMS is going to be developed.

In our work GC-MS was selected as method because it is more powerful for separation of arsenolipids especially arsenic-containing long chain hydrocarbons and arsenic-containing fatty acids. Methods for the identification of arsenolipids by GC-MS are developed so far, but quantification of those compounds in real samples is restricted due to the lack of suitable clean-up methods. Before quantification with GC-MS, it is important to clean up the sample and increase the concentration of arsenic compounds.

Herein we report a determination of arsenolipids found in fish oil, from which they were separated by partitioning between hexane and aqueous methanol and then the aqueous methanol layer purified by cation exchange chromatography (50W-H<sup>+</sup>) using methanol/ammonia as eluent and final quantification with GC-MS.

Key words: arsenic, arsenolipids, fish oils, GC-MS, clean-up

**A-25**

**STABILITY STUDIES OF PHEOPHYTIN AND ITS ZINC(II) AND  
COPPER(II) COMPLEXES TO UV-B IRRADIATION BY VIS  
SPECTROSCOPY**

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Investigation of the stability of one chlorophyll derivative, pheophytin and its heavy metal complexes to continuous UV-B irradiation, were studied by VIS spectroscopy. The irradiation was performed in a photochemical reactor "Rayonnet" in 95% ethanol for different irradiation periods providing possibilities for the kinetic analysis; the total measured energy flux (hitting the samples) was about  $12.0 \text{ Wm}^{-2}$  at 10 cm distance from the UV-B lamps. The stability of pheophytin (MP) and its Zn(II) and Cu(II) complexes (Zn-Pheo and Cu-Pheo, respectively) to continuous UV-B irradiation was studied by absorbance spectroscopy. The chosen pheophytin, Zn- and Cu-Pheo complexes undergo decomposition (degradation) obeying first-order kinetics. The stability of pheophytin, Zn(II)- and Cu(II)- pheophytin complexes to UV-B irradiation is ordered as Zn-Pheo < Pheo < Cu-Pheo (Cu-Pheo complex is the most stable). According to the results obtained from this work, heavy metal in the central position of pheophytin structure seems to play a significant role in stability of Zn(II) and Cu(II) complexes of Pheo to UV-B irradiation - affinity of heavy metals to four nitrogen atoms in the center of porphyrin molecule could play a role of the stability factor (for heavy metal complexes) against UV-B irradiation.

Key words: pheophytin, copper, zinc, complexes, UV-B irradiation

## A-26

# DETERMINATION OF LYCOPENE IN RED DRIED TOMATO BY UV-VIS AND FTIR SPECTROSCOPY

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Lycopene is one of the most important and useful carotenoid found in nature, and a potent antioxidant that has been shown to play critical role in cancer prevention. The investigations were studied on red dried tomato samples (produced by Agrova-Skopje) dissolved in three different solvents: methanol, acetone and chloroform and pure lycopene (produced by BUROV EOOD). The investigations were carried using UV-Visible and FTIR spectroscopy.

UV-Vis spectra showed spectral peaks at 444.0 nm, 470.9 nm, 501.96 nm and 503.0 nm for lycopene found in extracted red dry tomato for all solvents. Intensity of absorbance depends on the type of solvent.

FTIR spectra obtained for red dry tomato showed spectral peaks characteristic for functional groups for pure lycopene at  $3220\text{cm}^{-1}$  for C-H str. ( $\text{sp}_2$ ),  $2918\text{cm}^{-1}$  for C-H str. ( $\text{sp}_3$ ),  $1650\text{cm}^{-1}$  for C=Cstr. (Trans),  $1423\text{cm}^{-1}$  for  $-\text{CH}_2$  (Bending),  $1031\text{cm}^{-1}$  for C-H(Trans),  $672\text{cm}^{-1}$  for  $\text{R}_2\text{C}=\text{CR}$  for pure lycopene.

Concentration of characteristic functional groups of lycopene contained in pure capsule and red dry tomato is followed by FTIR spectroscopy. Dependence between concentration of characteristic functional groups and time of dissolution is also established. Intensity of absorbance depends on the type of solvent.

The outcome of study shows that the FTIR and UV method are good analytical methods for determination of lycopene in red dry tomato.

Keywords: Red dry tomato, Lycopene, FTIR, UV-Vis spectroscopy

**A-27**

**RAMAN AND INFRARED STUDY OF TEMPERATURE AND UV LIGHT  
INDUCED DENATURATION OF DNA**

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Micro-Raman and FT-IR spectroscopy was applied to study the changes in structure of isolated DNA as a function of temperature and UV light.

DNA was isolated from animal liver according to the method from Alexander and Griffiths. After tissue homogenization and proteolytic digestion, SDS (sodium dodecyl sulfate) was used as a detergent for cells lysis, while a solution of chloroform/isoamyl alcohol (24:1) as an agent for protein denaturation. Finally, cold ethanol was added for DNA precipitation. DNA purity was controlled using UV/Vis spectroscopy.

Micro-Raman spectra were recorded on a micro-Raman spectrometer LabRam 300 (Horiba Jobin-Yvon) (in 100–4000  $\text{cm}^{-1}$  spectral region) using He-Ne laser line (632.8 nm). Solid DNA was placed on a microscopic glass and temperature was monitored by temperature controlled heating stage in the temperature interval between 25 °C and 90 °C. FT-IR spectra were recorded in 600–4000  $\text{cm}^{-1}$  spectral region, on an ATR Golden Gate cell, using high stability temperature controller in the 25 °C to 90 °C temperature interval.

Both, Raman and infrared spectra of DNA showed strong and defined vibrational bands at room temperature. Increasing of temperature caused broadening of the bands, shifting in frequency, and for some of the bands, pronounced intensity changes. The results were discussed in terms of three temperature regions: (i) premelting (25–70 °C); (ii) melting (70–80 °C) and (iii) post melting (above 80 °C).

An attempt was also made to follow (a) the UV light induced degradation of DNA and (b) vitamin C role as a DNA protecting agent. Raman spectra of water solutions of DNA after their UV radiation (at 254 nm) in different time intervals were recorded. The same procedure was used with different concentration of vitamin C added in the DNA solutions. The extent of degradation of the DNA under the prolonged UV light was discussed.

**Keywords:** Raman spectroscopy, FT-IR spectroscopy, DNA, temperature and UV light degradation

A-28

**CHARACTERIZATION OF URINARY BIOACTIVE PHENOLIC METABOLITES EXCRETED AFTER CONSUMPTION OF A CUP OF MOUNTAIN TEA (*Sideritis scardica*) USING LIQUID CHROMATOGRAPHY – TANDEM MASS SPECTROMETRY**

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A nutrition experiment was performed for studying the bioavailability of polyphenols from *Sideritis* with healthy human subjects, who consumed a standardized *Sideritis* decoction after which urine was collected and analyzed. 35 polyphenolic compounds in the ingested decoction and 63 of their metabolites in urine collected after ingestion were identified using HPLC/MS<sup>n</sup>. It was shown that phenolic compounds present in *Sideritis* decoction are extensively conjugated to glucuronides, sulfates and also transformed to methylated forms after oral administration. Upon ingestion, the  $\beta$ -glycosides are hydrolyzed by microbial  $\beta$ -glycosidase resulting in formation of the aglycones hypolaetin, methylhypolaetin, isoscutellarein, methylisoscutellarein and apigenin, which are subsequently absorbed in the gut and transported to the liver.

In the analyzed urine samples, 31 different metabolites of hypolaetin, methylhypolaetin, isoscutellarein, methylisoscutellarein and apigenin, and 32 phenolic acids metabolites were detected, hypolaetin and isoscutellarein metabolites being the most abundant. This enabled polyphenols metabolites patterns to be obtained, which is a crucial step towards revealing the bioavailability and metabolism of phenolic compounds from *Sideritis* in human. The identification and structure elucidation of these metabolites provided essential data for further studies of *Sideritis* polyphenols bioavailability and pharmacokinetics.

Keywords: *Sideritis*, mountain tea, flavonoids, polyphenols, metabolites, bioavailability

**A-29**

## **SEQUENTIAL INJECTION ANALYSIS OF ANIONIC SURFACTANTS USING A POTENTIOMETRIC DETECTOR**

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Keywords: microfluidics, sequential injection analysis, anionic surfactant, model, effluent

Sequential Injection Analysis (SIA), the second generation of Flow Injection Analysis (FIA) techniques, was used in these investigations for determination of anionic surfactants (AS) in diluted detergent formulations, used as model effluents.

A flow through home-made potentiometric detector, implemented into a home-made SIA system, recorded the electromotive force changes as a function of the investigated AS concentration. Sodium dodecyl sulfate and sodium dodecyl benzenesulfonate were used for the calibration purpose. The specific software was developed for the data acquisition and elaboration, as well as for the instrument control. The detector exhibited almost Nernstian response toward the surfactants investigated down to  $10^{-6}$  M. A 1,3-didecyl-2-methylimidazolium-tetraphenylborate ion-pair was applied as electroactive material in the detector sensing element.

Sample and reagent injection as the initial input parameters were investigated and optimized. A special attention was paid to the controlled dispersion process as well as to the reproducible timing. The standard addition methodology was used for testing the method, whereas the potentiometric titration was used as a reference method. The described SIA device was tested in stopped-flow mode too.

Key words: Sequential Injection Analysis, Flow Injection Analysis, anionic surfactants, model effluents.

**A-30**

**OPTIMIZATION AND METHOD VALIDATION FOR ASSAY  
DETERMINATION OF DOXYCYCLINE, OXYTETRACYCLINE AND  
TETRACYCLINE IN PHARMACEUTICAL PRODUCT**

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Tetracyclines are broad spectrum antibiotics and very commonly used to treat acne and skin infections; systemically for infections of the respiratory, urinary and gastrointestinal tract. A method for assay determination of doxycycline (DOX), tetracycline (TC) and oxytetracycline (OTC) respectively, in a final pharmaceutical product was optimized and validated. Extraction with several mediums such as water, ethanol, methanol and 0.1M HCl, was tested. The water was chosen as solvent because of its availability; it is more ecologically-friendly and cheaper solvent. Sample treatment involves simple extraction with the solvent, ultrasonic treatment and suitable dilution after filtration. The assay was determined UV-spectroscopically, with a VARIAN Carry Win 50 UV/Visible spectrophotometer, in a 1-cm cell at wavelength range 190 - 500 nm, with resolution 0.5 nm and scan rate of 300 nm/min.

Each method was validated according to the ICH quality guidelines, *i.e.* the guideline for Validation of Analytical Procedures Q2 (R1). All the tested parameters were within the tolerated limits for assay determination, from 98% to 102%. The LOD of 0.4 µg/ml (DOX), 0.8 µg/ml (TC) and 0.57 µg/ml (OTC) and LOQ of 1.3 µg/ml; 2.4 µg/ml and 1.68 µg/ml, respectively, were calculated. A high linear correlation between the obtained detector signal is confirmed with high correlation coefficient of 0.9995 (DOX); 0.9997 (TC) and 0.9996 (OTC) expressed as average values of the measured absorbances of the standard solutions of DOX, TC and OTC in the range from 0.7 – 15 µg/ml; 0.4 - 60 µg/ml and 0.8 – 40 µg/ml, respectively. Recovery was shown to be good in all cases, ranging from 98.08 to 101.67 %, which excludes the possibility of interference of the components of placebo with the absorbance curve of each of the tetracycline and the accuracy of the method is confirmed. For determination of the precision of the method, the assay test was performed ten times, preparing separate test solutions using same homogeneous sample expressed as RSD with value of 1.53% for DOX; 3.53% for TC and 3.85% for OTC.

The presented methods offer the simplicity needed testing a large numbers of samples in a short period of time, necessary for routine analyses. The tested specimens include: DOKSICIKLIN caps. 100 mg; MEDOCYCLINE caps. 100 mg; NEOSULFOX P oral powder; and GEOMYCIN soluble powder.

Keywords: assay, validation, UV spectrophotometry, Doxycycline, Tetracycline, Oxytetracycline

## A-31

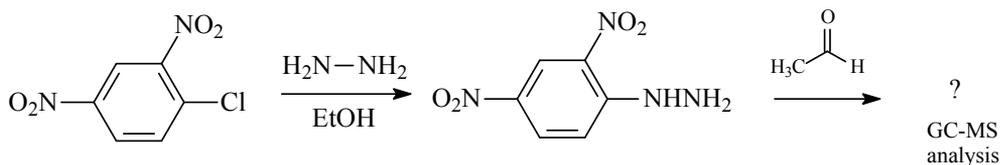
## CLASSICAL METHODS VERSUS MODERN CHROMATOGRAPHIC METHODS FOR IDENTIFICATION OF ALDEHYDES

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In the course of the past several years we have made efforts to modernize our organic chemistry lab courses by introducing/incorporating modern instrumental methods (IR, GC, MS) of analysis. Gas chromatography is a quite powerful tool available to the practicing chemist for qualitative and especially quantitative analysis and is a staple instrument in most of the laboratories around the world. A gas chromatograph coupled to mass spectrometer (GC-MS) is unrivaled for qualitative analysis of small volatile organic compounds (especially if mass spectral libraries are available). With the emergence of several GC-MS instruments at our institute and the demand of qualified personal in the country as a whole, we have decided to incorporate these techniques in our undergraduate curriculum. To fully utilize the power of GC-MS besides the knowledge of analytical chemistry, a sound knowledge of organic chemistry is needed. Herein we describe a discovery-based experiment in which students, by applying GC-MS analyses discover the identity of all products formed in the reaction between 2,4-dinitrophenylhydrazine and acetaldehyde. In the first lab (3-4 hours) the student prepares the 2,4-dinitrophenylhydrazone (2,4-DNPH, Brady's reagent) via a nucleophilic aromatic substitution reaction between 1-chloro-2,4-dinitrobenzene and 85% hydrazine hydrate. Both the starting material and the product are analyzed by TLC, mp, mixed mp IR, and GC-MS. In the next period a 2,4-dinitrophenylhydrazone derivative of an aldehyde (acetaldehyde) is prepared and analyzed the classical way (mp) and set aside. The student prepares aqueous solution of acetaldehyde and prepares a 2,4-dinitrophenyl hydrazone derivative with slight excess of 2,4-DNPH. Upon extraction and subsequent work-up the student prepares the sample for GC-MS analysis. After the analysis the student is given a print out of the chromatogram and the mass spectra of each of the observed peaks. The student then identifies the unreacted starting material and products and assigns their structures based upon retention times and analysis of mass spectral fragmentation patterns.



Key words: aldehydes, ketones, 2,4-dinitrophenylhydrazine, 2,4-dinitrophenylhydrazone, GC/MS.

**BIO, FOOD AND PHARMACEUTICAL CHEMISTRY AND TECHNOLOGY (BFP)**

## BFP - 1

### ULTRASOUND ASSISTED EXTRACTION OF FRUCTO-OLIGOSACCHARIDES, TOTAL PHENOLIC AND FLAVONOID COMPOUNDS FROM FRUITS AND VEGETABLES

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Diet rich in fruit and vegetable has been proven to reduce the development of a considerable number of chronic diseases, such as cancer and cardiovascular diseases. This protective effect has been attributed to the high concentrations of functional compounds. In this context prebiotic oligosaccharides as well as total phenolic and flavonoid compounds play significant role.

The aim of this study was to examine the content of fructo-oligosaccharides (FOS), as well as total phenolic (TPC) and flavonoid compounds (TFC) in selected fruits and vegetables. Ultrasound assisted extraction of functional compounds in blueberry, nectarine, raspberry and watermelon from the fruits and Jerusalem artichoke, garlic, spring garlic, leek, white onion and scallion from the vegetables was performed in different solvents. Methanol was found to be best extraction solvent. Fruits contained lower amount of FOS compared to vegetables, on the other hand, TPC and TFC were found to be higher in fruits. Highest concentration of total FOS was detected in white onion, 6.61 g/100 g fresh weight of edible sample. Blueberry showed the highest amount of TPC (112.6 mg GAE/g fresh weight) and TFC (93.6 mg CE/g fresh weight).

Cluster analysis was applied to categorize the fruits and vegetables according to their FOS, TPC and TFC content. Raspberry and blueberry from the fruits formed statistically significant cluster reach in total phenolic and flavonoid compounds, while onion and spring garlic, from the vegetables formed statistically significant cluster reach in oligosaccharides.

Key words: fructo-oligosaccharides, phenolics, flavonoids, fruits, vegetables

## BFP-2

# PRESSURE EQUILIBRATION AFTER VACUUM IMPREGNATION OF APPLE TISSUE STUDIED BY GAS IN SCATTERING MEDIA ABSORPTION SPECTROSCOPY (GASMAS)

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Vacuum impregnation (VI) is a unit operation in which a porous tissue is immersed in a solution. Vacuum is applied to the system provoking the flow out of the internal air trapped in the extracellular spaces of the tissue. Upon restoration of the atmospheric pressure, the external liquid flows into the pores replacing the air. In this paper, apple pieces were vacuum impregnated with isotonic sucrose solution (18 % w/v) for different times and reduced pressures (15, 30, 45 kPa (abs.)). Using GASMAS (Gas in Scattering Media Absorption Spectroscopy) it was possible to observe that apples, in which air has not been totally exhausted during the impregnation operation, keep an internal reduced pressure which rises slowly toward ambient over a time scale of hours. Both the residual vacuum and the timescale of pressure equilibration with ambient varied with applied vacuum level and apple variety. This phenomenon might be a direct consequence of the topology, geometry and hydrophobicity of the complex matrix of intercellular spaces in the tissue.

Key words: vacuum impregnation, pressure equilibration, GASMAS, apple

**BFP-3****FORMULATION AND PROCESS OPTIMIZATION OF SOLID LIPID NANOPARTICLES PREPARED BY HIGH SHEAR HOMOGENIZATION TECHNIQUE**

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The aim of the present study was to optimize the formulation and process parameters for preparation of solid lipid nanoparticles (SLN) and to evaluate their influence on mean particle size (nm) and particle size distribution (SPAN factor) of aqueous and freeze-dried SLN samples.

High shear hot melt emulsification method (Ultra-turrax<sup>®</sup>T25, Ika-Werke, Germany) was used for preparation of aqueous SLN dispersion (*sample 1*). Optimization of formulation embraced altering the concentration of phospholipid (Lipoid<sup>®</sup> S100) (0.8 – 2.0% w/w), maintaining at the same time constant concentrations of lipid phase (10% w/w Witepsol<sup>®</sup> W35) and co-emulsifier (0.4% w/w sodium glycocholate). Process optimization parameters covered homogenization time (2, 5 and 7 min), speed (17500 and 24000 rpm) and dispersion volume (15 and 30 ml). Prepared SLN were subsequently freeze-dried (Labconco, USA). Evaluation of the influence of two cryoprotectants, sucrose (*sample 2*) and trehalose (*sample 3*), on SLN particle size and particle size distribution was performed. Concentration of both cryoprotectants was 10 % w/w. Six-month stability studies were carried out at 25±2 °C/60±5%RH and 5±3 °C (*Köttermann, Germany*).

Using 10 % w/w Witepsol<sup>®</sup> W35, 0.4 % w/w sodium glycocholate, and phospholipid (Lipoid<sup>®</sup> S100) (0.8 – 2.0% w/w), SLN with diameter of 130 to 179 nm and particle size distribution of 1.547 to 2.778 were prepared. Increased emulsifier concentration resulted in decreased particle size, reaching the lowest point at 1.4% (w/w) ( $d_{50} = 130$  nm) and SPAN factor of 1,547. Subsequent higher emulsifier concentration resulted in larger particles (179 nm), most likely due to multilayer formation on particle surface and/or liposome formation. Optimal process parameters were: homogenization time – 7 min, homogenization speed - 24000 rpm and sample volume - 15 ml ensuing SLN particle size of 130 nm and particle size distribution of 1,547. Free flowing powders were procured by freeze drying (*sample 2* and 3). Freeze-dried SLN rapidly re-dispersed in water by ultrasonication. Particle size and SPAN factor were 128 nm and 1,527 and 129 nm and 1,793 for *sample 2* and 3, respectively. *Sample 1* manifested slight increase in mean particle size (137 nm) during six-month stability studies at 25 °C, while particle size distribution was not altered at all. *Sample 2* stability studies pointed to increased particle size (283 nm) and SPAN factor value (2,576), while *sample 3* at the same time exhibited remarkable instability and increased mean particle size to micrometer range. Stability studies carried out at 5 ±3 °C indicated that prepared SLN are not stable at this storage conditions.

Key words: solid lipid nanoparticles, high shear homogenization, mean particle size, particle size distribution.

## BFP-4

# LEAD CONTENT DETERMINATION IN SOME DECORATIVE COSMETIC PRODUCTS

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Samples of lipsticks, lip glosses and eye shadows were analyzed in this study. In order to obtain a wider color palette and better shine, some mineral pigments, dye and shimmers are added to these preparations. These auxiliary components may contain certain metals (Al, Zn, Si, Ti, Pb) as their integral part or as contaminant. As these preparations are applied directly to the lips and skin, they could be potential sources of heavy metals in the human body.

In this study, decorative cosmetics products were analyzed. Regarding to cumulative and toxic effects of lead, the influence of auxiliary components (mineral pigments, dye and shimmers) on the total content of this heavy metal is observed.

Lead content in the analyzed samples was determined using potentiometric stripping analysis (PSA).

The content of lead in the tested samples of lipsticks ranged from 26.83 to 105.64  $\mu\text{g/g}$ , with the highest content in a shimmering pink lipstick. Other researchers have also shown that shimmering lipsticks had much more lead content compared to lipsticks without this auxiliary component, indicating that the shimmers can be one of the sources of lead in lipsticks.

Samples of lip glosses showed for about 2 to 8 time lower lead content than analyzed lipsticks. This difference in the content of lead between these products, may be due to the fact that higher amount of coloring additives are added to lipsticks compared to lip glosses.

Eye shadows with added shimmers, as well as samples of lipsticks, contain more lead (53.19 - 95.55  $\mu\text{g/g}$ ) in comparison to eye shadows without this component (26.43 - 50.41  $\mu\text{g/g}$ ).

Results of this study indicate that the cosmetics that are used for aesthetic purposes can have adverse effects due to the fact they contain a highly toxic metal lead, the content of which varied depending on the added auxiliary components.

Key words: lipstick, lip gloss, eye shadow, lead, PSA

## BFP-5

### INFLUENCE OF THE STORAGE ON ANTIOXIDANT ACTIVITY AND SENSORIAL PROPERTIES OF HERBAL LIQUEUR

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The antioxidant activity of a commercial herbal liqueur "Bitter 54", Serbian domestic brand and its sensory attributes were studied during one year storage under various conditions. The antioxidant activity was evaluated using the DPPH test. The samples were subjected to sensory evaluation using the internal sensory panel of Faculty of Agriculture, University of Belgrade where five attributes were evaluated: color intensity, clarity, bitter taste, odor intensity and herbal-fruity taste. The sensory properties were presented on a twenty-point scale. Freshly prepared herbal liqueur "Bitter 54" (sample B54 first day of experiment) was compared with samples stored in original packaging (opaque green bottles) in cardboard box (B54), in the original packaging with the presence of air (bottles filled to half capacity, without cover, in a cardboard box (B54A), in the original packaging exposed to the effects of daylight (B54GL) and in bottles of white transparent glass exposed to daylight (B54WL). All samples were kept at ambient temperature.

Storage of commercial herbal liqueur "Bitter 54" in the original packaging (B54) during the experiment reduced antioxidant activity by over 20 %. This decrease was most pronounced in the first 150 days of the experiment and then stagnated. Samples B54GL and B54WL reduced the antioxidant activity after one year for 6 % and 18 %, respectively. Student's *t*-test showed that there was no statistically significant difference ( $p < 0.05$ ) between the antioxidant activity of samples kept in the dark with and without the presence of oxygen. This is probably due to negligibly small amounts of oxygen from the air that could be dissolved under existing conditions, without mixing or additional oxygen. Freshly prepared beverage had excellent quality and kept it during the first months of the storage under adequate storage conditions. Good quality of B54 lasted till the end of the storage, while variations in quality of samples stored under various conditions were significant and time-dependent.

Key words: herbal liqueur, antioxidant activity, sensorial properties, storage

## BFP-6

### PROPERTIES OF PROTEINS FROM HEAT AND MICROWAVE TREATED DEOILED RICE BRAN

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Protein is a key ingredient that contributes to the nutritional value, flavor and functional properties of different food formulations. Functional properties of proteins are determined by their physicochemical properties and the structure. Rice bran is underutilized by-product of brown rice milling. It is valuable source of high-quality hypoallergenic proteins, but also lipids, dietary fibers, vitamins and minerals. Utilization of rice bran as food is limited because of lipid hydrolysis and subsequent oxidation during storage. This makes the stabilization treatment an important step for their further usage. The changes in protein structure during stabilization and defatting affect the changes of functional properties. Solubility of proteins, an important characteristic for their possible use as food ingredient, is directly related to foaming and emulsifying properties.

The objective of this study was to investigate the properties of proteins isolated from a mixture of rice bran obtained by three steps of rice milling. In order to inactivate lipases equal portions of rice bran were treated with heat for 20 minutes at 120 and 140°C, and with microwaves for 10 minutes at same temperatures. The treated samples and untreated ones were defatted using n-hexane. Proteins were extracted from deoiled samples with alkaline treatment (pH 9) followed by precipitation. The protein yield varied due to treatment type and temperature. The percentage of protein recovery was higher at increased temperature, and particularly in microwave treated samples. Protein isolates had minimum solubility in pH range between 6 and 8, and maximum solubility at pH 12. The foaming capacity of rice bran proteins increased with pH, but obtained foams had poor stability. Emulsifying capacities examined at pH 6 were higher for samples treated at lower temperature. The protein from untreated sample showed the highest emulsion forming capacity, compared to proteins from heat treated rice bran and those treated with microwaves that had the lowest emulsifying capacities.

Key words: Rice bran, protein isolates, solubility, foaming, emulsifying

## BFP-7

### RESEARCH ON THE DEGRADED ARTIFACTS FOR THE DEVELOPMENT OF NEW PROTECTION METHODS

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The colonization of the artifacts by harmful microorganisms is known as biodeterioration. The emergence of microorganism colonies and biodeterioration are often related to environmental conditions. The most important factors affecting microbial growth are the physical ones (especially humidity, temperature and light) and chemical nature of the substrate. Among colonies producing the biodeterioration of the artifacts, many species of deuteromycete (*Alternaria* sp., *Aspergillus* sp., *Fusarium* sp., *Hemicola* sp., *Myrothecium verrucaria*, *Penicillium* sp., *Stachybotrys atra*, *Stemphylium* sp., *Trichoderma* sp., *Ulocladium* sp., etc.) and ascomycete (*Chaetomium* sp.) are frequently isolated from books, documents and printings. Fungal infestation can lead to very rapid degradation of organic artifacts, fully affecting inorganic artifacts too. Fungi of the genus *Aspergillus* are among the most prevalent and are responsible for many of the biodeterioration effects observed.

It must be noted that fungi (particularly *Aspergillus* sp.) affect the support materials of different types, starting from ceramic, wood, paper, through to textiles, paintings (wall or canvas) and even metals. Basically, fungi grow on any material that can provide the necessary nutrients (organic matter). However, fungi can grow on inorganic materials, obtaining nutrients from surface or airborne material.

Various methods can be applied for the removal of the microorganism affecting the artifacts. However, one question remains: how to prevent the reborn of the microorganism?

One answer would be the complete isolation of the artifacts. However, this method cannot be always applied. We propose the formation of transparent films on the surface of the objects that would prevent contact with the atmosphere. The paper presents some aspects regarding the steps involved in the restoration and conservation of some selected artifacts.

Keywords: biodeterioration, artifacts, protection methods

## BFP-8

### NATURAL EXTRACTS FOR SOLVING THE ISSUE OF BIODETERIORATION OF THE ARTIFACTS

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The biodeterioration of the artifacts (historical buildings or archaeological objects) is a worldwide problem. Cultural heritage of each country is practically an act of identity and how it is preserved is an important indicator of the degree of civilization and awareness of its significance. Internationally, UNESCO (United Nations Educational, Scientific and Cultural Organization) is having among its objectives the conservation of the world cultural heritage. Currently, there are 936 World Heritage sites (725 cultural, 183 natural and 28 mixed) in 153 countries. Each of these sites is considered important for the international community. We all have a moral duty to preserve evidence of past civilizations for the future generations.

The exposure of the artifacts (including building materials) to environmental conditions (temperature, pH, humidity, aerobic or anaerobic conditions, etc) can lead to mould growth. The growth and development of microorganisms on the artifacts makes their conservation more difficult and for these reasons adequate interventions must be taken to stop or at least slow down the biodeterioration process. The moulds can deteriorate objects through the formation of patina with different colors (from dark to green) or crusts. They are able to produce different elements (aluminum, calcium, potassium) through bio-solubilization process, elements which can produce other damages like salts solubilization.

The most common fungal species found on contaminated objects belong to genera of *Aspergillus*, *Penicillium*, *Cladosporium*, and *Aureobasidium*.

The aim of this investigation was the valorification of some natural selective extracts from plants native in Romania with antifungal properties for biological decontaminations of artifacts.

Key words: natural extract, biodeterioration, historical building, artifacts

## BFP-9

### TREATMENT OF DAIRY INDUSTRY WASTEWATER BY BIOAERATION

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Wastewaters from milk production and processing are characterized by high biodegradation of organic pollutants (ratio  $_{20^{\circ}\text{C}}\text{BOD}_5/\text{COD}$ ), often 70% or more. In this respect, the subject of this paper is the application of biochemical aerobic waste water treatment with the aim to increase the efficiency of recovery of organic matter. Basically, it is necessary to perform mechanical wastewater treatment, and after that air insufflation into equalization tank in order to prevent the deposition of suspended matter and anaerobic processes. After the physical-chemical treatment, wastewater is discharged into the bio-aeration tank with active sludge where extended aeration is being performed. This activity triggers the nitrification process. In the secondary sludge precipitator, the sludge is being recirculated into bioaeration tank and drained for further processing. Wastewater treated in this way is discharged into the chlorination pool, after which it can be discharged into rivers with large ecological requirements.

Key words: dairy industry, waste water, bioaeration.

**BFP-10**

**PROJECT SOLUTION FOR WASTE WATER TREATMENT IN  
MEAT PROCESSING INDUSTRY**

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The qualitative characteristics of the waste water originating from meat production and processing are organic pollution which include blood, proteins, fats, small cuts of meat, etc. The pollution assessment can be monitored through the specific parameters such as  $_{20^{\circ}\text{C}}\text{BOD}_5/\text{COD}$  and suspended organic matter. Pollution of these waste waters depends on the degree of blood recovery, the size of the slaughterhouse, and the method of evacuation of fecal matter. The paper presents the criteria of change in production technology, which involves the recovery of blood and complete evacuation of fecal matter, but also the project solution for wastewater pre-treatment plant in meat processing industry. First of all, waste waters are accumulated in a collecting tank, which allows the treatment to take place in a continuous flow, and after that, the materials from the technological process are removed through a fine grating. These raw materials are being moved to the container where the material removed by sieve is being stored, and then further processed with other waste materials from production processes in the rendering plants. Wastewater is discharged into the reactor for intensive physical-chemical treatment in which air flotation is performed by adding  $\text{Ca}(\text{OH})_2$ ,  $\text{FeCl}_3$ ,  $\text{Al}_2(\text{SO}_4)_3$  and ultra sterile water which contains a sufficient amount of chlorine to disinfect wastewater. In the container, flotation material is being processed with other waste materials from the technological process of production. The water treated in this way is being drained into the aeration reactor, leveling the pH using  $\text{Ca}(\text{OH})_2$ , and eliminating ammonia as a gas. This process is followed by pH adjustment using  $\text{H}_2\text{SO}_4$ . Ammonia absorption by  $\text{H}_2\text{SO}_4$  is performed in the scrubber, and we obtain  $(\text{NH}_4)_2\text{SO}_4$  (which can be used in agriculture) and effluent – treated collective waste waters from production activities of meat processing of meat, which are discharged into the city sewers.

Key words: meat processing industry, waste water, treatment.

**BFP-11**

**ESTIMATION OF DIETARY INTAKE OF ARSENIC, CADMIUM AND LEAD  
THROUGH INFANT AND BABY FOODS MARKETED IN THE VOJVODINA  
PROVINCE, SERBIA**

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Arsenic, cadmium and lead are toxic elements. These elements cause adverse health effects in humans, especially in infants since their intestinal absorption is significantly higher than in adults. Therefore, it is desirable to quantify their levels in commonly consumed infant foods. The main aim of this study was to determine the arsenic, cadmium and lead concentration in infant and baby foods marketed in the Vojvodina Province, Serbia, and to estimate the potential health risk to the youngest children through the daily consumption of the studied infant foods. The element contents of selected infant foods collected from the market in the city area of Novi Sad (the capitol of the Vojvodina Province) were determined using graphite furnace atomic absorption spectrometry (GF-AAS) after microwave digestion of samples. The obtained levels of investigated contaminants in different types of infant food were used to calculate the daily intakes. Dietary intakes of these potentially toxic elements were assessed in comparison with the data published in the literature.

Key words: toxic elements, young children, GF-AAS, daily intake

## BFP-12

# USE OF COMMERCIAL SODIUM HYPOCHLORITE SOLUTIONS IN RESPECT TO THE QUALITY OF THE PRODUCTS

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Sodium hypochlorite is the most popular solution for root canal irrigation in stomatology practice. NaOCl ionizes in water into hypochlorite ion  $\text{OCl}^-$ , establishing equilibrium with hypochlorous acid (HOCl). In acidic and neutral media, HOCl exists predominantly, whereas at pH 9 and above,  $\text{OCl}^-$  predominates. Hypochlorous acid is responsible for the antibacterial activity. Being strong oxidant it is effective disinfectant which disrupts several vital functions of the microbial cell, resulting in cell death. In concentrations between 0.5% and 6% it is a potent antimicrobial agent, killing most bacteria instantly on direct contact.

The aim of this study was to investigate the possibility of using some bleach solutions for root canal irrigation.

Because of its low price, bleach is widely used in Macedonia. Alkaloid AD Skopje produces 10% and 20% sodium hypochlorite disinfectant solution that is used in the food industry. The Varakina bleach which is a solution of sodium hypochlorite with a scent of lemon is used for whitening laundry and bed linen. The samples of commercial solutions were taken from the market and tested for the presence and concentration of heavy metals as impurities. The atomic absorption spectrophotometry (AAS) is used for determination of heavy metals in tested solutions.

Results were compared to the German code standard which allows not more than 20 ppm of heavy metals in hypochlorite solutions used for irrigation.

The obtained results showed that the concentrations of heavy metals in the tested samples were below maximal allowed concentrations for the tap water.

It can be concluded that commercial solutions can be used for root canal irrigation but only after checking the quality of the product for the content of heavy metals as impurities. It is recommended to use purified water to obtain desired dilution. However, it is always safer to use products specially designed for stomatological use than commercial sodium hypochlorite products aimed for other purposes.

Key words: hypochlorite solutions, root canal irrigation

**BFP-13****KINETICS MECHANISM OF ENZYMATIC MODIFICATION OF QUERCETIN  
WITH CYSTEINE BY HORSERADISH PEROXIDASE**

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Quercetin (3,3',4',5,7-pentahydroxyflavone) is the most studied of the dietary flavonoids and one of the most abundant plant-derived polyphenol, which possesses numerous biological and pharmacological effects including antioxidant, antimutagenic, anticarcinogenic, antimicrobial, and antiinflammatory properties. Previous studies have shown that the oxidation of quercetin by oxidative enzymes such as peroxidases resulted in three major oxidation products, which could react with various nucleophilic agents building adducts. The objectives of this study were to investigate the enzyme modification of quercetin with L-cysteine by horseradish peroxidase, and to evaluate the kinetic mechanism of enzymatic modification of quercetin, as well as to determine the values of kinetic parameters  $K_m$ ,  $V_{max}$  and  $k_{cat}$  for substrates, and the proportion of enzymatic reaction in overall reaction. Reaction of modification of quercetin was followed by recording of spectral changes over time at 380 nm. All reactions were performed in 100 mM phosphate buffer pH 6.0 at 20°C. Kinetic parameters were determined graphically from the linear Michaelis-Menten equation. Values were obtained at intervals:  $V_{max} = 0.17 \div 0.91 \Delta A_{380} \cdot \text{min}^{-1}$ ,  $K_m = 0.023 \div 0.5 \text{ mM}$ ,  $k_{cat} = 0.21 \div 1.14 \Delta A_{380} \cdot \text{min}^{-1} \cdot \text{nM}^{-1}$  and  $V_{max}/K_m = 0.83 \div 26.55 \Delta A_{380} \cdot \text{min}^{-1} \cdot \text{mM}^{-1}$ . As for the kinetic characterization of the modification reaction of quercetin with L-cysteine, the results indicate that the reaction is mostly enzymatic with less part non-enzymatic. These experiments indicate that the reaction with peroxidase have a higher rate compared with the reaction without horseradish peroxidase. The part of non-enzymatic reaction is about 10% of the total reaction. It has been found that all studied reactions of the modification of quercetin with L-cysteine by horseradish peroxidase take place following certain order. We propose that horseradish peroxidase initially reacts with hydrogen peroxide, then with quercetin, and finally with L-cysteine which further leads to the introduction of L-cysteine into the structure of quercetin.

Keywords: horseradish peroxidase, quercetin, cysteine, kinetic mechanism, spectrophotometry

**BFP-14**

**THE ANTIOXIDANT ACTIVITY OF CHAMOMILE FLOWERS  
(*MATRICARIA CHAMOMILE L.*)**

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Chamomile and its extracts are used in the pharmaceutical industry for their antispasmodic, antiinflammatory and antimicrobial properties. The composition of chamomile consists of mostly lipophilic and hydrophilic compounds. Flavone apigenin, a compound with antiphlogistic and spasmolytic activities, accumulates in white ligulate flowers of the anthodium in the form of apigenin-7-O- $\beta$ -glucoside and its acylated derivatives.

In the present study extracts of tetraploid chamomile ligulate flowers were examined. In order to obtain a product-extract with higher spasmolytic activity, apigenin-7-O- $\beta$ -glucoside was transformed into apigenin using  $\beta$ -glucosidase present in chamomile. The higher content of apigenin in the fermented flowers (F-CLF) compared to unfermented (CLF), was determined using TLC methods.

Owing to the content of phenolics and flavonoids, the chamomile extracts obtained with different solvents (ethanol, methanol, water) possess antioxidant activity. DPPH assay was used as a free radical-scavenging method and it has been found that the methanolic and ethanolic F-CLF extracts exhibit  $IC_{50}$  value of 0.127 g/ml and 0.094 g/ml, respectively. These results are better than those for CLF. The extracts were capable of reducing  $Fe^{3+}$ , and thus capable of donating electrons.  $EC_{50}$  value for CLF, determined by reducing power method, was higher than that for F-CLF extract.

Key words: chamomile, apigenin, antioxidant activity, phenols, flavonoides.

## BFP-15

# ANTIBACTERIAL ACTIVITY OF TMPO AND ITS COMPLEXES WITH TRANSITION METALS

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Intensive studies in recent years showed that some nitroxyl radicals and its derivatives possess certain biological activity. It is considered that practically all radicals can be isolated and stabilized using various methods. Presently, the problems of determination of concentration and studies on reactivity stand before the researchers. In biological media, versatile unstable radicals are formed the significance of which is not fully clarified in a number of physiological and pathological processes. Certain free radicals are so stable that they can persist under conditions close to these of ordinary chemical compounds. The stable iminoxyl (nitroxyl) radicals of the series of tetramethylpyridines and tetramethylpyrrolidines, as spin labeled probes, spin labels and paramagnetic models of biologically active models, are often used in various studies in the field of biology, medicine, physics, chemistry, etc.

Bactericidal substances affect microbial cells through different mechanisms: after penetration in the cell, the substance initiates protoplasm coagulation; bactericidal substances inhibit the catalytic effect of catalytic systems after penetration on the cells; many bactericidal substances are accumulated onto cell wall thus disturbing cell metabolism.

The present announcement studies the antibacterial activity of TMPO (2,2,6,6-tetramethyl-4-aminopiperidyl-1-oxyl) and its complexes with ions of molybdenum, vanadium, zinc and copper. The complexes were obtained in aqueous solutions of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  at room temperature. The complexes were characterized by elemental analysis, FT-IR and electron paramagnetic resonance. The experiments on antibacterial activity were carried out in the concentration interval 2.0-0.01 mg/ml at 37°C for 24 h. The minimal inhibiting concentrations of the substances tested for *Escherichia coli* were determined. The highest antibacterial activity showed the complex TMPO+Zn (MIC 0.062 mg/ml), and the lowest was that of TMPO+Mo (MIC 1.0 mg/ml). Comparative experiments were carried also with Rifamicin SV.

Keywords: TMPO- complexes, *E. coli*.

## BFP-16

# DETERMINATION OF LEAD AND CADMIUM IN INFUSION SOLUTIONS AND SOLUTIONS FOR HEMODIALYSIS

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Parenteral solutions for hemodialysis, solutions for the correction of electrolyte disbalance and fluid replacement are often used in treatment of severe clinical diseases and conditions in medical practice. These solutions may directly through injection, or indirectly after application into the body cavity reach the bloodstream, so it is essential that they are sterile, isotonic, apyrogenic and non-toxic.

The aim of his study was to determine the content of toxic heavy metals lead and cadmium in infusion solutions and solutions for hemodialysis. The presence of these metals was determined using highly sensitive microanalytical technique potentiometric stripping analysis (PSA).

Lead content in the infusion solution (NaCl, Hetasorb 6%) ranged from 2.89 to 6.05  $\mu\text{g/L}$ , while the content of lead and cadmium in the dialysis solution was 27  $\mu\text{g/L}$  and 4.17  $\mu\text{g/L}$ , respectively.

Considering that these solutions entered directly into the bloodstream, or that they are indirectly in contact with blood and other body fluids, it is necessary to monitor the content of these toxic metals. This is particularly important in cases where these solutions are used for a longer period (hemodialysis), when the harmful and toxic effects of these metals are pronounced and can effect patient clinical condition.

Key words: infusion solutions, solutions for hemodialysis, lead, cadmium, PSA

## BFP-17

### ACTIVITY OF STRESS RESPONSE REGULATORS IN *ESCHERICHIA COLI* TO TREATMENT WITH SUBLETHAL DOSES OF THYMOL

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Essential oils (EO) are known to possess antimicrobial activity against a wide spectrum of microorganisms. Thymol (5-methyl-2-(1-methylethyl)-phenol), found in thyme, isomer of carvacrol, is a component commercially used for a long time and is active against *E. coli*, *S. aureus*, *L. monocytogenes*, *C. jejuni*, *S. enterica*, but also against insects. The cellular defense mechanisms and stress responses of microorganisms toward phenolic components of essential oils (PCEOs) are poorly known, in contrast to the defense mechanisms against conventional antibiotics which have been described in detail for *Escherichia coli*.

In this research, a library of *E. coli* cells with green fluorescent protein (*gfp*) inserted to RpoE, RpoH, RpoS, LexA or RcsA stress promoter is used in order to measure their transcriptional activity during treatment with sublethal doses of thymol. This gave some answers on the cellular defense mechanisms and stress responses of *E. coli* toward PCEOs and provides information's concerning the safety of food treated with EO. The implications of this for food processing are that one sublethal processing stress may produce preadaptation to a series of other stresses and increase survival through further processing stages.

The cells were grown for 4 hours at 37 °C in a SynergyH4 multi-well fluorimeter (Multi-Mode Microplate Reader, Biotek) with sublethal dose of thymol while OD and fluorescence emission were measured at 600nm and 535nm, respectively. Expression profiles are presented as the plot of GFP over OD with time. High temperature and starvation assays were done on cells treated with thymol for exploring the preadaptation effect.

From the experimental data it can be concluded that except for RpoS, all other promoters have altered expression profiles during cell growth at sublethal dose of thymol. Surprisingly, some of the stress promoters are less transcribed in the cells treated with thymol then in the controls. This is most obvious for the RcsA promoter which after 3.3 hours from the thymol addition has 12.2 – 14.8% and 8.9-10.5% decrease of transcription in cells treated with 0.4 and 0.9mM, respectively. The only significant increase in promoter transcription during treatment with both 0.4 and 0.9mM thymol was found for LexA having 14.4-21.1% and 11.4-14.6% increase, respectively.

Keywords: thymol, sublethal doses, stress promoters, *E. coli*

## BFP-18

# COMPARISON OF THE RHEOLOGICAL AND BREDMAKING QUALITIES OF SOME WHEAT CULTIVARS FROM KOSOVO IN PRODUCTION OF BREAD

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The main grain that is used in Kosovo is the wheat. The main cultivars that are cultivated are those of soft wheat (*Triticum aestivum L.*) which is used in production of bread, and the bread accounts for the main daily consumed product in Kosovo. The major parts of the cultivars that are used originate from the countries of former Yugoslavia, and a minor part of it originates from Europe. The latter differ a lot in terms of technological qualities. The study encompasses some types of wheat cultivars which are predominantly cultivated in Kosovo, mainly for bread production. The quality of wheat and the rheological properties of the dough were analyzed.

The results of the rheological qualities indicate that the dough obtained from cultivar Pobeda has the best rheological qualities for bread production. It has a softening degree of 70 FU, energy 77.3 cm<sup>2</sup> and maximum viscosity of 550 AU. Cultivars “Evropa” and “Lenta” indicate positive rheological bread making qualities, whereas cultivar “Luna” indicates poor rheological quality with a softening degree of 145 FU, energy of mere 28.7 cm<sup>2</sup> and maximum viscosity of 320 AU. Furthermore, based on the analysis of the breads obtained from the wheat, one can observe that the breads produced from cultivars “Pobeda”, “Evropa” and “Lenta” have better quality than bread produced from “Luna” cultivar.

Key words: wheat, rheological qualities, Lenta, bread.

## BFP-19

# TOTAL POLYPHENOLS, FLAVONOID CONTENT AND ANTIOXIDANT CAPACITY OF COMMERCIALY AVAILABLE FRUIT TEAS IN SERBIA

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Tea phenolic compounds, tea polyphenols, constitute 50-70% of tea water extract and have been regarded as the quality parameters or indicators of tea. Nowadays, consumption of tea is part of people's daily routine. Numerous studies have demonstrated that the aqueous extract of the major tea polyphenols possesses antimutagenic, antidiabetic, antibacterial, anti-inflammatory and hypocholesterolemic qualities. Analysis of tea is an effective method for the determination of tea quality. The objective of our research was to evaluate the total polyphenols, flavonoid content and the antioxidant activity of ten fruit tea samples from Serbian markets. The total polyphenol content was determined spectrophotometrically according to the Folin-Ciocalteu method ( $\lambda=760$  nm), using gallic acid (GA) as a standard, and ranged from 4.83 mg GAE/g (blueberry tea) to 81.91 mg GAE/g (pomegranate tea). The total flavonoid content in selected fruit tea samples was determined according to the aluminum chloride spectrophotometric method ( $\lambda=510$  nm). Catechin was chosen as a standard and the results were expressed in milligram catechin equivalents per gram of tea extract (mg CE/g). Results ranged from 16.49 mg GAE/g (forest fruit tea) to 31.64 mg GAE/g (raspberry tea). DPPH radical scavenging activity, 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) radical cation scavenging activity (ABTS), ferric reducing-antioxidant power (FRAP) and reducing power assay Fe(III) to Fe(II) (RP) were used to assess the antioxidant capacity (AC) of fruit teas. These assays, based on different chemical mechanisms, were selected to take into account the wide variety and range of action of antioxidant compounds present in selected tea samples. All samples showed antioxidant power, but a wide range of ACs was observed. The results obtained in this work are generally consistent with literature data.

Key words: total phenols, flavonoids, antioxidant capacity, fruit teas

## BFP-20

# TOTAL POLYPHENOLS, FLAVONOID CONTENT AND ANTIOXIDANT CAPACITY OF COCOA PRODUCTS

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Polyphenols in cocoa have potent antioxidative activities *in vitro* and *in vivo*. Drinking cocoa is not only a treat for the tongue; it may also have some tangible benefits for heart health, such as lowering blood pressure slightly. Recent research has also indicated that the polyphenols found in cocoa and dark chocolate are associated with short- and long-term health benefits including oxidation of LDL cholesterol, reduced platelet aggregation and increased arterial blood flow. The aim of this research was to evaluate the total polyphenol and flavonoid content as well as antioxidant activity of five cocoa products from major commercial manufactures in Serbia. The Folin-Ciocalteu reagent was used to determine total polyphenols ( $\lambda=760$  nm). Gallic acid (GA) was used as a calibration standard and the data were expressed as milligram gallic acid equivalent per gram of cocoa (mg GAE/g). This study showed that the total phenolic content in the selected cocoa samples ranged from 3.82 to 36.87 mg GAE/g. The total flavonoid content was determined according to the aluminum chloride spectrophotometric method ( $\lambda=510$  nm). The data were expressed as milligram catechin equivalent per gram of cocoa (mg CE/g). Total flavonoid content from different cocoa samples ranged from 2.02 to 10.82 mg CE/g. The antioxidant capacity (AC) of cocoa samples were analyzed using four different assays based on different chemistry: DPPH radical scavenging activity, 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) radical cation scavenging activity (ABTS), ferric reducing-antioxidant power (FRAP) and reducing power assay Fe(III) to Fe(II) (RP). All samples had different antioxidant capacities in relation to the method applied. The results obtained are in agreement with literature data.

Key words: total phenols, flavonoids, antioxidant capacity, cocoa

## BFP-21

### USE OF RAPD “FINGERPRINTING” TECHNIQUE TO DETECT GENOTOXIC EFFECTS OF HEAVY METALS IN PLANTS

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Metals constitute one of the major groups of genotoxic environmental pollutants possessing serious threat to human as well as environmental wellbeing. Heavy metals induce several cellular stress responses and damage different cellular components, proteins, membranes and DNA. “DNA alterations” include DNA damage (e.g. DNA adducts, breaks), mutations (e.g. point mutations and large rearrangements) and other possible changes (e.g. structural distortion) induced by chemical or physical agents. Random Amplified Polymorphic DNA (RAPD) ‘fingerprinting’ technique is based on the amplification of genomic DNA with 10 bp primers of arbitrary nucleotide sequence which anneals to multiple regions of the genomic DNA. The PCR reactions thus generate many amplicons of variable lengths (e.g. between 100 and 4000 bp) which can be separated by gel electrophoresis to obtain DNA fingerprint. RAPD assays were successfully used to detect genetic instability in DNA alterations in animals, bacteria and plants induced by low doses of pollutants, heavy metals among them also.

The objectives of this study were to detect DNA damage in plants induced by different metals using the RAPD technique. Plant samples of selected medicinal plants from the industrialized area were taken from different places between 10-100 m around the lead smelting plant “MHK Zletovo” in Veles, while for uncontaminated controls, plant samples were taken from Plačkovica Mountain, about 60 km from the city of Veles. Different plant organs (leaves, flowers, radix and stems) were analyzed by ICP-AES (Varian715-ES) for selected metals. Detection of genotoxic effect using RAPD involves the comparison of profiles generated from control (unexposed) and treated (exposed) DNA. Events observed following the metal exposure were a variation in the disappearance and appearance of new bands. These unique bands clearly differentiated the samples exposed to heavy metal stress, and could act as a marker for assessment of environmental exposition of these metals.

Key words: heavy metals, RAPD, DNA damage, plants

**BFP-22**

**MINERAL NUTRIENT IMBALANCE, TOTAL ANTIOXIDANT LEVEL AND  
DNA DAMAGE INVOLVED IN TOXICITY IN *PHASEOLUS VULGARIS L.*  
SEEDLINGS EXPOSED TO METAL IONES**

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The present study aimed to analyze the biological effects induced by bioaccumulation of metals, Cu, Cd, Pb, Zn, Ni and Mn in model plant (*Phaseolus vulgaris L.*, *Fabaceae*). Effects of mineral nutrient imbalance, total antioxidant level and DNA damage induced by heavy metals were investigated in bean seedlings treated with two concentrations of 150 and 350 mg L<sup>-1</sup> of selected metals for seven days. The results demonstrated that the increasing metal concentration changed synchronously metal content in samples, decreased total antioxidant activity (assessed by Ferric-Reducing Antioxidant Power – FRAP assay) in all samples with exception for samples treated with Ni and Cd. DNA damages were investigated by Random Amplified Polymorphic DNA (RAPD) method. The results demonstrated that the increasing metal concentrations induced changes in RAPD profiles (disappearance and/or appearance of bands in comparison with untreated control samples). The highest number of missing bands was observed in samples treated with zinc (total 4 bands) and nickel (total 4 bands) at both concentrations. These results suggested that mineral nutrient imbalance is involved in changes of antioxidant levels and DNA damages of the seedlings, which may help to understand the mechanism of metal toxicity in plants.

Key words: toxicity, heavy metals, antioxidants, *Phaseolus vulgaris*, RAPD, FRAP

## BFP-23

# DETERMINATION OF SELENIUM IN FOOD SUPPLEMENTS BY USING SPECTROPHOTOMETRIC METHOD

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A simple and low cost spectrophotometric method is optimized for selenium determination in food supplements. Variation of single parameter method was used for the optimization of the method of analysis. The methodology is based on the reaction of selenium with iodine ions in acid medium in the presence of amides. Free iodine is released in solution, which reacts with amides by giving a violet color in sample solution. The measurements were performed at  $\lambda_{\max} = 574 \text{ nm}$  ( $\epsilon_{\max} = 144660 \text{ Amol}^{-1}\text{cm}^{-1}$ ) in 1 cm glass cell. The performance, sensitivity and accuracy of this method are very high. To avoid the interferences of the matrix in the determination of selenium the standard addition method has been used which has a high performance and a linear calibration graph with a very good linearity coefficient  $R^2 = 0.9996$ .

The food supplement samples (2 different food supplements) were chosen randomly in different pharmacies in Tirana (5 samples for each food supplement). The selenium concentration per tablet ranged from  $25.38 \pm 1.47 \text{ }\mu\text{g/tablet}$  to  $54.86 \pm 1.36 \text{ }\mu\text{g/tablet}$ .

The selenium concentration determined in the analyzed samples is within the range of the concentration declared in the patient information leaflet for both food supplements ( $25 \text{ }\mu\text{g/tablet}$  and  $55 \text{ }\mu\text{g/tablet}$ ) analyzed by the pharmaceutical companies.

The accuracy of the analysis was checked by recovery of the spikes which was in the range of 97-102%. The method yielded reproducible results with  $\text{RSD} < 4.66\%$ .

Key words: spectrophotometry, food supplement, selenium concentration, calibration graph, coefficient of linearity

## BFP-24

### DETECTION OF HISTAMINE IN FOOD STUFF USING SCREEN-PRINTED CARBON ELECTRODES MODIFIED WITH RHENIUM (IV) OXIDE

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Biogenic amines are low molecular nitrogenous compounds with biological activity, usually formed by the microbial decarboxylation of amino acids. Food containing large amounts of biogenic amines can have toxicological consequences. One of the most active biogenic amine and most frequently involved in food-borne intoxications is histamine. The electrocatalysed oxidation of histamine on a screen printed electrodes was investigate for the purpose of its amperometric determination in flow injection analysis. Histamine is oxidized by the mediator, which in turn is re-oxidized electrochemically. The resulting histamine sensor showed a linear dynamic range up to 10 mg/L with a detection limit ( $3\sigma$ ) of 0.9 mg/L ( $E = -0.1V$ ) and 0.4 mg/L ( $E = -0.15V$ ), respectively. The repeatability was 5.7 % RSD ( $n = 10$  measurements), the reproducibility 14 % ( $n = 5$  sensors).

Key words: histamine, rhenium dioxide, amperometric determination, sensor

## BFP-25

# RELATION BETWEEN SOIL CHARACTERISTICS AND IRON CONTENT IN VIRGINIA TOBACCO

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The study was conducted on alluvial-meadow, maroon-forest soils and vertisols with Virginia tobacco. The total content of iron was measured through decomposition with HF, HClO<sub>4</sub> and HNO<sub>3</sub> acids. A solution of 0.005M DTPA + 0.1M TEA, pH 7.3 was used for extraction of the elements' mobile forms from soils. The preparation of plant samples was made by means of dry ashing and dissolution in 3M HCl. An atomic-absorption spectrometer "Spektra AA 220" of the Australian company Varian was used for determination of iron content in the soil and plant samples. Certified reference materials (three soils and one tobacco leaves) were also analysed for the verification of the accuracy of Fe determination.

The accumulation of iron in roots and shoots of tobacco plants have been studied. A correlation and regression analysis was conducted between pH, humus content, total and mobile forms of Fe in the soil and the concentration of the element in the root and the aboveground biomass of Virginia tobacco. The concentration of iron was highest in the roots.

It was established that there are no statistically significant dependencies determined between humus content, total iron in soil and Fe concentration in the plant organs of Virginia tobacco. The exponential model adequately reflects the relationship between soil pH and iron concentration in leaves of three harvesting zones. Regressional dependencies of great significance were determined between the mobile iron in the soil and the element concentration in the roots and leaves of the lower and middle harvesting zones.

Key words: Virginia tobacco, iron, soils

**BFP-26**

**ANTIOXIDANT AND ANTIMICROBIAL ACTIVITY OF ESSENTIAL OIL  
FROM DILL (*ANETHUM GRAVEOLENS* L.) SEEDS**

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Dill (*Anethum graveolens* L.) is an aromatic annual or biennial herb species from the genus *Anethum* of the family *Apiaceae* (*Umbelliferae*). It is well known as medicinal herb with antimicrobial, hypotensive, antihyperlipidemic, diuretic, antiemetic, laxative and spasmolytic effect. The medicinal part is the seed, the fresh or dried leaves and the upper stem. Dill seed consists of dried fruit of *Anethum graveolens*. Whole seeds and crushed fruits are used to make teas and other galenic formulations for internal application. Dill seeds contain 2-5% essential oil, the major constituent of which is carvone (20–60%).

The essential oil from dill seeds was obtained by hydrodistillation in a Clevenger-type apparatus. The highest yield of oil, after five consecutive hydrodistillation runs, was obtained by the technique in which water from still flask was separated by filtration and used together with fresh water for immersing the plant material in a subsequent distillation. The essential oil composition was determined by HPLC analysis. Disc diffusion test was used to determine the antimicrobial activity. Antibacterial and antifungal activity was tested against five laboratory control strains of bacteria and one strain of yeast. The best antimicrobial activity of essential oil from dill seeds was detected against *Staphylococcus aureus*. The essential oil exhibited significant activity against other microorganisms. The antioxidant activity of essential oil is determined by DPPH test. The antioxidant activity of essential oil increased with increasing essential oil concentration. The results show that obtained essential oil can be used as a natural antioxidant and antimicrobial agent, and it can be used in pharmaceutical and cosmetic industry.

Key words: dill (*Anethum graveolens* L.), essential oil, hydrodistillation, antioxidant activity, antimicrobial activity.

## BFP-27

# ANTIBACTERIAL ACTIVITY OF TWO RASPBERRY (*RUBUS IDAEUS* L.) CULTIVARS

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*Rubus idaeus* L. (raspberry) is one of the most famous Serbian fruit. Serbia is one of the largest manufacturers and exporters of raspberries in the world. Between 90 and 95% of cultivated raspberries in Serbia are from “North American Willamette” cultivar, which is characterized by the excellent taste and a dark red colour. Besides the Willamette, the “Meeker” cultivar is also present. Raspberry is rich in phenolic compounds such as phenolic acids, flavonoids and anthocyanins. Raspberry is not only available fresh, but frozen and processed into juice, jam, ice cream and wine. Because of the biological properties associated with berry fruits, the identification of their antimicrobial activity was the objective of this study. The strains tested belong to reference and wild strains: *Staphylococcus aureus*, *Staphylococcus saprophyticus*, *Bacillus cereus*, *Bacillus* sp., *Listeria monocytogenes* (Gram-positive bacteria), *Escherichia coli*, *Pseudomonas aeruginosa*, *Salmonella typhimurium* and *Salmonella* sp. (Gram-negative bacteria). Extracts from whole berries were tested in concentration of 50 mg/ml by disc diffusion method (using 15 µl of extracts) and agar-well diffusion method (using 50 µl and 100 µl of extracts). The least activity of raspberry extracts for all tested bacterial strains was obtained by disc diffusion method, where the inhibition zones of about 7 mm were found only against few bacteria. Tested extracts in amount of 50 µl had an inhibitory activity against all tested bacteria, of which the most susceptible strain on “Meeker” cultivar was *Salmonella typhimurium* and on Willamette cultivar was *Staphylococcus aureus*. Antibacterial activity increased in parallel with the increasing the extracts volume, so by applying 100 µl of extract volume, inhibition zones are higher for about 3-5 mm. Raspberry extract from “Willamette” cultivar (in amount of 100 µl) showed higher antibacterial activity against *Escherichia coli*, *Pseudomonas aeruginosa* (both reference and wild strains), *Bacillus cereus* and *Bacillus* sp. than those from “Meeker” cultivar. Of all tested strains *Escherichia coli* was the most resistant strain with only zones of reduced growth, while other strains showed clear zones, which could indicate the bactericidal activity.

Key words: Willamette cultivar; Meeker cultivar; antibacterial activity; reference strains; wild isolates

**BFP-28**

**COMPARATIVE ANALYSIS OF ORGANIC AND CONVENTIONAL MILK**

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With the advent of industry and modernization in the world there have been changes in the human diet. They are used in various synthetic means to make food last longer, have better taste, smell, color, etc. All this has led to ask: is the quality of food satisfactory, if all the substances used in production and in food are really necessary and have they adverse effects on human health?

Many studies show that certain substances added to food or used for its protection have a negative impact on human health, and that the conventional production for years destroys nature, exhausts its resources and undermines human health. All this has led to the late twentieth century phenomenon "new direction" in food production so called "organic". "Organic" production is based on traditional food production, which differs from conventional production and maintains a balance with nature.

The aim of this this paper is to recognize the basic characteristics of organic food and its production, in particular organic milk that is produced in Montenegro. In addition, one of the aims of this paper is to describe the benefits of organic over conventional milk and its nutritional significance. The analysis displayed the benefits of organic milk production over conventional milk production when it comes to human health and protection of the environment.

For the purpose of this paper the the content of major elements, trace elements and heavy metals, as well as the presence of nitrate and nitrite, both in raw organic and conventional milk were determined. These findings served to answer the question if organic milk is better for consumption.

Key words: organic milk, conventional milk, trace elements, major elements, heavy metals.

## BFP-29

### EVALUATION OF DPPH, FRAP, FRP ANTIOXIDANT ACTIVITY OF THIRTEEN DIFFERENT STRAWBERRY CULTIVARS

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Strawberries are worldwide consumed fruit, both as fresh and as ingredient in processed products. Besides their unique flavor, it is now well known that strawberries present a rich source of antioxidant compounds such as vitamin C, carotenoids and phenolic compounds including anthocyanins. The intake of antioxidants present in food is an important factor in health protection and has been found to offer protection against these diseases. Dietary flavonoids are expected to have an important role in the prevention of coronary heart disease, cancer, and neurodegenerative diseases. Phenolic compounds, especially bioflavonoids are becoming of increasing importance in science, because of their antioxidant activity. Flavonoids can reduce oxygen and nitrogen free radicals, by donating hydrogen atoms by virtue of the reducing properties of the multiple hydroxyl groups. Strawberry (Alba, Hana, Asia, Queen Elisa, Marmolada, Apolo, Roxana, Senga, Faveta and Clery) cultivars were analyzed for total phenols, total anthocyanin content and antioxidant activity. Total polyphenol content was determined spectrophotometrically according to the Folin-Ciocalteu method ( $\lambda=760$  nm), using gallic acid (GA) as a standard, and ranged from 141.15 mg GAE/g (Asia) to 263.01 mg GAE/g (Alba). Anthocyanins ranged from 13.87 mg C3GE/100 g (Queen Elisa) to 25.98 mg C3GE/100 g (Alba). Antioxidant activity was determined as radical scavenging activity (DPPH), ferric ion reducing power (FRP), ferric ion reducing/antioxidant power (FRAP) and trolox equivalent antioxidant capacity (TEAC). Cultivars Alba and Apolo had the highest antioxidant activity measured by all assays. The results obtained in this work are generally consistent with literature data.

Keywords: total phenols, anthocyanins, antioxidant activity, strawberry cultivars.

## BFP-30

### PHENOLIC PROFILES OF COMMERCIAL DARK BEERS FROM SERBIA

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This study examined total phenolic content (TPC) and individual phenolic compounds in commercial dark beers consumed in Serbia. Phenolic compounds are generally considered as one of the very important antioxidant sources in beer. The TPC of beer was determined according to the Folin-Ciocalteu spectrophotometric method. The measurement was compared to a calibration line of prepared gallic acid (GA) solution, and the results were expressed as milligrams of gallic acid equivalents (GAE) per liter of beer (mg GAE/L). Ten phenolic compounds including gallic acid, protocatechuic acid, 4-hydroxybenzoic acid, 2,5-dihydroxybenzoic acid, vanillic acid, caffeic acid, p-coumaric acid, ferulic acid, sinapic acid and salicylic acid were identified in beer samples. Identification was carried out by comparing the retention times and spectral data with those of standards. Quantitative determination of individual phenolic compounds in beer was calculated using calibration lines. Results were expressed as milligrams per litre of beer (mg/l).

Key words: beer, total phenolic content, phenolic acids.

**BFP-31**

**ANTIOXIDANT ACTIVITY OF SIX APPLE CULTIVARS IN SERBIA**

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Apples have been identified as one of the main dietary sources of antioxidants, mainly phenolic compounds. These compounds vary in their composition and concentration among cultivars and fruit tissues. In this research, the total phenolic content (Folin-Ciocalteu assay) and total flavonoid content were studied. Total antioxidant capacity (TAP) of selected apples were analyzed using 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) radical cation (ABTS), 2,2-diphenyl-1-picrylhydrazyl radical scavenging capacity (DPPH), ferric ion reducing power (FRP) and ferric ion reducing antioxidant power (FRAP). Among cultivars, 'Granny Smith' apple has a significantly higher content of total phenolics (178.72 mg GAE/100g f.w.) and of total flavonoids (124.24 mg CE/100g f.w.). High phenol content was significantly correlated with high antioxidant capacity.

Keywords: phenolics, flavonoids, antioxidant capacity, apple.

**BFP-32**

**TOTAL ANTIOXIDANT CAPACITY OF CERTAIN MEDICINAL PLANTS  
ASSESED WITH FRAP METHOD AND CYCLIC VOLTAMMETRY**

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Antioxidants are substances that protect cells from damage caused by free radicals. Many of the biological properties, including antimutagenic, anticarcinogenic and antiaging, among others, may originate from antioxidant property of many substances. Plant phenolic compounds (e.g. phenolic acids, flavonoids, quinones, coumarins, lignans, stilbenes, and tannins), nitrogen compounds (alkaloids, amines), carotenoids and vitamins are the most important plant substances possessing antioxidant activity.

The aim of this study was to analyze the total antioxidant levels of medicinal plants collected in the region of Malesevo Mountain, by two different methods and compare the results.

Infusions used as samples were prepared from: *Origanum vulgare* L. (mountain tea), *Mellisa officinalis* L. (lemon balm), *Hypericum perforatum* L. (St. John's wort), *Thymus serpyllum* L. (wild thyme) and *Mentha piperita* L. (mint tea).

The total antioxidant capacity (TAC) of herb infusions was evaluated using the FRAP method (Ferric reducing/antioxidant power; photometric method) developed by Benzie and Strain.

The total antioxidant capacity of these medicinal plants has also been studied in an ethanol/water phase by means of cyclic voltammetry (electrochemical method), by measuring the rate of the homogeneous redox reaction with ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid)).

The results from the FRAP method showed that mountain tea has the highest total antioxidant capacity 27.45. Next in the line are: lemon balm, with TAC value of 19.54, St. John's wort, 12.64, wild thyme, 9.45 and mint tea, 8.14. The results are expressed as  $\text{mmol Fe}^{2+} \text{L}^{-1}$ .

The results obtained with the voltammetric technique confirm the same trend of descending of the anodic current as the TAC values in analyzed infusions.

As a conclusion we can say that total antioxidant levels in infusions prepared from medicinal plants originated from our country exhibit strong antioxidant potential, and this fact justifies their use as potent natural antioxidant agents.

Both photometric and electrochemical methods can be used for assessment of total antioxidant levels in medicinal plants infusions.

Key words: antioxidant capacity, plants, FRAP, cyclic voltammetry

**BFP-33****COMPARISON OF DIMETHYLSULFOXIDE, GLYCEROL, AND ETHYLENE GLYCOL AS CRYOPROTECTIVE AGENTS FOR NITRIFYING AND DENITRIFYING STRAINS**

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Our laboratory has a collection of over 1500 isolates of microorganisms. The majority of the microorganisms were segregated from soil and from wastewater, and are kept in paraffin. The aim of this work is to examine the effect of the three chosen cryoprotectants (DMSO-dimethyl sulfoxide, glycerol and ethylene glycol) on the process of freezing a few nitrifying (*Nitrosomonas* 4N<sub>2</sub> and *Nitrobacter* 7N<sub>2</sub>) and denitrifying (*Pseudomonas* D<sub>3</sub>, *Pseudomonas* B 6-3, *Pseudomonas* INB 228 and *Pseudomonas* 5) bacteria. The examined bacteria have been isolated from wastewater. The isolated strains were inoculated on agarose medium, and a choice of the most appropriate colonies is made. These chosen insulators are transferred to an appropriate nutrient broth and are incubated for 24 to 48 hours at a temperature of 37°C. After the incubation period a mixture is made consisting of 1 ml of each bacterial suspension and 100 µl from the appropriate cryoprotectant. The prepared eppendorf tubes are left at room temperature for 1 hour, then to 4 °C for 1 hour and are eventually frozen at -20 °C. At the same time, a series of dilutions is prepared, and 1 ml from the dilutions (10<sup>-4</sup>, 10<sup>-5</sup> and 10<sup>-6</sup>) is transferred into empty petri dishes in which nutritious agar is diffused. These petri dishes are used to determine the CFU/ml of the bacteria before the freezing. After 8 months the process is repeated, but this time in a reverse order of events. The eppendorf tubes are gradually defrozed and are transferred to 4 °C for 1 hour and then at room temperature for 1 hour. For the prepared - incubated cultures, CFU is determined according to the process which has already been described. After being defrozed, the number of viable cells of *Nitrosomonas* 4N<sub>2</sub> with glycerol is 79.81%, with DMSO it is 23.37%, whereas with ethylene glycol is 3.55%. The number of viable cells of *Nitrobacter* 7N<sub>2</sub> is 81.74% with glycerol, 68.24% with DMSO and 9.52% with ethylene glycol. The number of viable cells of denitrifying bacteria, *Pseudomonas* D<sub>3</sub>, *Pseudomonas* B 6-3, *Pseudomonas* INB 228 and *Pseudomonas* 5 with glycerole is 56.12%, 63.24%, 45.28%, and 59.48%, respectively; with DMSO is 49.62%, 71.29%, 40.72% and 27.58%, respectively; and the number of viable cells with ethylene glycol is 36.56%, 2.71%, 37.13% and 31.89%, respectively. From the results given, it can be concluded that the most effective cryoprotectant for nitrifying and denitrifying strains is glycerol (64.28 %), less effective is DMSO (46.81 %), and least efficient cryoprotectant is ethylene glycol (20.23%).

Key words: nitrifying strains, denitrifying strains, cryoprotectant

**BFP-34****GLYCEROL AS A CARBON SOURCE FOR ANTIBIOTIC PRODUCTION  
BY *STREPTOMYCES HYGROSCOPICUS* CH-7**J. Ćirić<sup>1</sup>, Slavica Ilić<sup>1</sup>, Sandra Konstantinović<sup>1</sup>, Vlada Veljković<sup>1</sup>, G. Gojgić-Cvijović<sup>2</sup>, Dragiša Savić<sup>1</sup>

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Species of the genus *Streptomyces* can grow and produce antibiotics on substrates containing different carbon sources. The actinomycete *Streptomyces hygroscopicus* produces a range of polyene antibiotic compounds (hexaene-H85 and azalomycine) depending on the cultivation conditions. In addition to the production of biodiesel, the crude glycerol is released in relatively large amounts (10% of the input quantities of oil). Crude glycerol has usually a purity of 80% and could be a starting raw material for the production of pure glycerol. However, the purification process is costly and often not economically justified.

The aim of this work was to study the possibility of antibiotic production by growing *S. hygroscopicus* CH-7 in a medium containing glycerol as a carbon source. Production of antibiotics was monitored in a laboratory using crude glycerol obtained from biodiesel production with rapeseed and sunflower oils. The microorganism was cultivated in 500 ml Erlenmeyer flasks fixed on a rotary shaker (150 min<sup>-1</sup>) at 28°C for 5 days. The concentrations of antibiotics were determined spectrophotometrically after extraction from the culture supernatant by proper solvents (ethyl-acetate for azalomycine and *n*-butanol for hexaene). Glycerol concentration was determined by HPLC.

*S. hygroscopicus* CH-7 produces different maximal amounts of antibiotics depending on the source of carbon:

Carbon source	Maximal concentration, µg/cm <sup>3</sup>	
	Hexaene	Azalomycine
Glucose	19.3	32.9
Pure glycerol	14.7	24.2
Sunflower oil glycerol	38.7	2.4
Rapeseed oil glycerol	12.0	10.4

The highest hexaene concentration was obtained in a medium with sunflower oil glycerol from biodiesel production, twice more than the amount when glucose was used as a carbon source. As opposed to hexaene, the bacterium produced the most azalomycine in a medium containing glucose, about 25% less in pure glycerol, and less in the medium with crude glycerol from biodiesel production.

The medium with sunflower oil glycerol from biodiesel production could be used as a promising medium for streptomycete cultivation and hexaene production.

Key words: *Streptomyces hygroscopicus*, glycerol, biodiesel

## BFP-35

# DETERMINATION OF ORGANIC ACIDS AND SACCHARIDES DURING THE FERMENTATION OF PETROVAC SAUSAGE (Petrovskà Kolbàsà)

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Petrovskà kolbàsà is a traditional dry fermented sausage produced in Bački Petrovac, province Vojvodina, Serbia. It has been produced for many years without any additives so it has a recognizable flavor, color and taste. Metabolic activity of lactic acid bacteria during the fermentation of the sausages leads to the formation of organic acids which have major impact on the safety and aroma formation. For that reason, the concentration of organic acids and saccharides were determined in Petrovac sausage produced in three different ways: from hot deboned meat fermented traditionally and from cold meat fermented both under traditional and industrial conditions. During 90 days of traditional fermentation and 45 days of industrial fermentation of Petrovac sausage, a total number of 28 samples was collected and analyzed by HPLC method.

The major fraction of organic acids in all analyzed samples was lactic acid, although, acetic and citric acid were also detected. Sausages made from hot deboned meat had higher initial concentration of lactic acid compared to sausages made from cold meat. On the other hand, the concentration of lactic acid at the end of the fermentation was the highest in the samples produced from cold meat and fermented under traditional conditions. The citric acid concentration increased during the fermentation of the sausages made of cold meat, while this value remained almost constant for the sausages made of hot deboned meat. Contrary to this, the concentration of acetic acid increased during all three fermentations and the highest concentration was achieved in the sausages made from hot meat. The concentration of glucose was much higher for the sausages made of hot deboned meat.

Key words: fermented sausages, organic acids, lactic acid, glucose

**BFP-36**

## **GROWTH KINETICS OF LIPID-PRODUCING FRESHWATER MICROALGAE ISOLATES**

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Biodiesel gained a lot of interest in the past years as the alternative for fossil fuels. Current commercial production of biodiesel involves transesterification of triglycerides found in oleaginous food crops. Microalgae are currently considered to be one of the most promising sources for biodiesel production. They are capable of producing up to 100 times more oil per unit area of land compared to sunflower or rapeseed.

One of the most important steps in the production of biodiesel is the selection of appropriate microalgae strains. For this reason, in this work 6 microalgae species were isolated from freshwater ponds near Leskovac (village Lipovica) and home aquarium. In order to determine grow rate, biomass production and lipid content isolated strains were transferred into BBM medium and cultivated on a rotary shaker (150 min<sup>-1</sup>) for 4 weeks (27°C, under continuous illumination). Algal growth was monitored by measuring optical density at 680 nm, while the biomass production was determined gravimetrically. Total lipids were extracted from dry microalgal biomass using a method of Bligh and Dyer.

The microalgae strains were preliminary identified by the morphology tests as representatives of the genera *Chlorococcum* (1 isolate), *Desmodesmus* (1 isolate), *Chlorella* (1 isolate) and *Scenedesmus* (3 isolates). *Chlorella* spp. showed the highest grow rate, while the slowest growth was observed in *Chlorococcum* spp. The determined lipid content of the analyzed strains was in the range of 11-46 % of their dry weight. The lowest lipid content (11%), as well as the lowest lipid production (0.16 g/l) was found for *Chlorococcum* spp. *Desmodesmus* spp. had the highest biomass production with the value of 1.80 g<sub>dw</sub>/l. Three strains of *Scenedesmus* spp. had different biomass production in the range of 0.93-1.66 g<sub>dw</sub>/l, while their lipid production was less variable and in the range of 0.37- 0.45 g/l. The best results of oil production were obtained for *Desmodesmus* spp. (0.61 g/l) and *Chlorella* spp. (0.55 g/l) suggesting that these species can be further examined for their potential use in biodiesel production.

Key words: biodiesel, freshwater microalgae, biomass, lipid content

## BFP-37

### DETERMINATION OF AFLATOXINS IN MILK AND DAIRY PRODUCTS

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Mycotoxins are toxic secondary metabolites of many saprophytic moulds that in humans and animals come through food infected with spores or fragments of mycelium. Aflatoxin B1 (AFB1) produced by the mould *Aspergillus flavus* is dominant in cereals and food products.

Aflatoxin M1 (AFM1) is a major metabolite of AFB1 which is found in milk obtained from animals who consumed food contaminated with AFB1. After entering the body, AFB1 may be *metabolized* by the *liver into a reactive epoxide intermediate* or be hydroxylated into the less harmful AFM1.

Tests were made in animal feed (corn, concentrate feeds), raw cow, sheep and goat milk from Bitola region, as well as commercial milk and dairy products.

Two methods were used to analyze aflatoxins, a bioluminescence method for AFB1 using Charm II 6600 Luminometer, and high pressure liquid chromatography (HPLC) for AFM1 using VICAM columns. A mixture of acetonitrile and methanol was used as a mobile phase in HPLC method. The mean values of AFB1 concentrations determined in 60 samples of animal feed (corn and concentrate) ranged from 4.49 ppb to 4.93 ppb. The only exception was the AFB1 concentration in silage, which was higher than 7ppb. The concentration of AFM1 in all types of raw milk was in the range from 0.01 to 0.05 ppb. Of the dairy products, 38 samples were analyzed including cheese, yogurt, sour cream and contaminated sour cream. The latter was stored for 25 days, and samples were analyzed at 1<sup>st</sup>, 15<sup>th</sup> and 25<sup>th</sup> day. The concentration of AFM1 in the contaminated cream increased gradually with time.

Key words: Mycotoxins, aflatoxin B1, aflatoxin M1, milk, dairy products

## BFP-38

# EFFECTS OF ORIGINAL HERBAL OILY COMPLEX ON NASAL MUCOSA DURING THE RHINITIS TREATMENT

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Concerning the fact that the inflammation of nasal mucosa (rhinitis) as a disease is treated with different pharmaceutical preparations, and based on the comparison of the results acquired after using available therapeutic options, the research in this study was directed to finding the right therapeutic options and to the effects of nasal product based on natural active compounds. The solution of this problem was possible by following up the changes on cellular level. That is the reason for choosing scanning electron microscopy as irreplaceable method with its advantages for tissue analysis. Therefore, the aim of this paper was using SEM to find irregularities on cell level in patients with livid mucosa on nasal cavity, in patients with allergic and non-allergic rhinitis, as well with atrophic rhinitis, before and after the treatment with selected herbal oily extracts. Diseased nasal mucosa was treated with standardized herbal complex with natural compounds in form of nose drops: the oily extracts of plantain (*Plantago lanceolata*), walnuts (**Juglandis folium**), calendula (*Calendula officinalis*) and essential oil of peppermint (*Mentha piperita*) in paraffin oil.

The characteristic changes were observed on cellular level during the treatment using microscopic analysis, which also has shown the effects of applied herbal nasal product. The treatment of herbal extracts in the form of nose drops during three weeks significantly influenced the recovery of respiratory epithel. During the treatment, nasal product caused transitory hyper secretion which was gradually reduced after stopping of treatment and the appearance of mucosa was better (pinkish and moisten). In patients with atrophic rhinitis, the lost of dryness of mucosa was observed, as well the appearance of better vascularise, which was the prerequisite for recovery of the all nasal tissues. Besides, the regeneration or generation of new ciliar cells was observed with more active cilia, as well the reduction of the number of goblet cells.

This preliminary study showed that the herbal oily complex is a good alternative to the commercial nasal drops on the basis of vasoconstrictors, which do not cure the disease but only facilitate the disease with consequences of nasal mucosa atrophy.

Key words: herbal complex, rhinitis, microscopy

**BFP-39**

## **PREDICTION OF GENOTOXICITY FOR SERIES OF THIOPHENES USING SELF-ORGANIZING MAPS**

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The testing of genotoxicity of different substances is performed in order to assess the potential of the compounds which may cause heritable damage or it could induce cancer in humans. Many short-term **in vitro and in vivo** assays to evaluate mutagenicity have been developed and some of them are being used routinely. Although these assays can generally be completed within a short period, their throughput is not enough to assess the large number of chemicals that exist in our environment without additional information on their safety. Computational (**in silico**) methods are the way forward for assessing the genotoxicity of large numbers of chemicals. Importantly, these methods will also contribute to the reduction of animal use.

In this study the potential of supervised self-organizing maps for classification of thiophenes according to their genotoxicity has been examined using data set composed of 147 structures. In order to simplify the interpretation of the results the classification model was build using simple one-dimensional and two-dimensional descriptors. Variable selection procedure as well as the network architecture optimization was performed using genetic algorithms.

Using this approach, models with good generalization properties were developed. The concordance of the best model was 87%, sensitivity 88% and specificity 83% with 10-fold cross validation. Validation of this model with external test set had the following performances: concordance 76%, sensitivity 35% and specificity 97%.

Key words: genotoxicity, thiophenes, classification, self-organizing maps.

## BFP-40

### MONOCYTES AS POTENTIAL BIOMARKERS FOR DETECTING AND MONITORING OF COLORECTAL CANCER

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Colorectal cancer (CRC) is very common worldwide with 850,000 developing it annually and 500,000 dying of the disease. Peripheral blood is one of the less invasive sample sources that can be intensively screened for CRC biomarkers. Peripheral blood monocytes (PBM) represent a reservoir of the inflammatory cells that contribute to disease progression by different means. When recruited into tumors from the circulation, the microenvironment can drive monocyte differentiation into either macrophages or dendritic cells. Tumor-associated macrophages (TAMs) are typically characterized as either “classically” activated tumoricidal and anti-angiogenic macrophages (termed as M1) or “alternatively” activated pro-tumorigenic and pro-angiogenic macrophages (termed as M2). Monocyte derived dendritic cells (DCs) are professional antigen presenting cells that raise the immune response against tumor.

The aim of this study was to discover a different gene profile of peripheral blood monocytes during CRC. This genetic profile is validated for its use as a diagnostic marker for CRC. Monocytes offer an advantage to be easy isolated from the peripheral blood and as a diagnostic test is suitable to be used for screening a large population. In this way, the accuracy, precision and linearity determined to give this test a maximal sensitivity and specificity.

Key words: peripheral blood monocytes, colorectal cancer, diagnostic marker

**BFP-41**

**MONITORING THE STABILITY OF DRIED APPLE PRODUCT OBTAINED  
BY OSMOTIC PRETREATMENT**

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The apple variety used in this study was Mutsu. The apple samples were cut with a special knife with thickness of 1 to 2 mm in the form of a disc with diameter of 18 mm. Osmotic pretreatment was performed in aqueous solution of sucrose with a concentration of 50%. After the osmotic pretreatment the apples were dried in air-dryer at 100°C. The dried apples were packed in small bags of metalized polypropylene under atmosphere of nitrogen and kept at room temperature in dry place. The stability of the product was monitored over 150 days in 15 days interval. The stability of the product was evaluated by the changes of water activity, color and texture.

The dried apples before packaging had water activity of 0.291, suitable for extended shelf life. The value of the browning index of the dried apples was 48.68 and the hardness was 3.88 N. After 150 days of storage the water activity was slightly increased to 0.342, which subsequently led to increased browning effect and softening of the tissue. The browning index reached value of 52.81, while the hardness of the dried apples decreased to 2.53 N. The changes of the color of the dried apples during storage were not significantly different. The texture on the other hand exhibited significant softening but was still acceptable for consumption.

Key words: osmotic dehydration, stability, water activity, color, texture.

## BFP-42

### EFFECT OF THE MEDIUM COMPOSITION ON THE *STREPTOMYCES HYGROSCOPICUS*'S MORPHOLOGY AND ANTIBIOTIC PRODUCTION

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The impact of modified media on the morphology of *Streptomyces hygroscopicus* as well as on the antibiotic production was studied. To make the production of the antibiotic feasible, it is necessary to optimize the production, which includes, among the other conditions, the optimization of the medium composition. The fermentation basal medium has the following composition (g dm<sup>-3</sup>): glucose 15, CaCO<sub>3</sub> 3, NaCl 3, MgSO<sub>4</sub> 0.5, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> 0.5, K<sub>2</sub>HPO<sub>4</sub> 0.5 and soybean 1.0. A part of soybean was replaced with an inclusion complex (0.5 g dm<sup>-3</sup>) in the modified medium. The fermentation medium was inoculated with a 48-hours old preculture (5% v/v) incubated at 30°C for 140 hours under the standard condition of aeration and agitation (200 rpm). A medium including inclusion complexes of isatin-Schiff bases with  $\beta$ -cyclodextrine was developed to maximize the production of antibiotics hexaene H-85 and azalomycine B by *Streptomyces hygroscopicus*. The medium with  $\beta$ -cyclodextrine inclusion complex of isatin-3-thiosemicarbazone resulted in the maximal antibiotic concentration of 493  $\mu\text{g}\cdot\text{cm}^{-3}$  for hexaene H-85 and 191  $\mu\text{g}\cdot\text{cm}^{-3}$  for azalomycine B. During the fermentation in the medium with inclusion complexes of isatin-Schiff bases, the bacterium was in the form of compact pellets, which were formed from short and long, branched filaments.

Keywords: *Streptomyces hygroscopicus*,  $\beta$ -cyclodextrine, inclusion complex, antibiotic production, morphology

## BFP-43

### THE CHEMISTRY OF BEER AGING IN ECONOMY TYPES OF PACKAGING

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The PET bottle has been challenging the entire European brewing industry and PET has mainly substituted the glass as a packaging material. The reason for this development is the price and excellent material properties of PET. On extremely competitive markets where beers do not only battle other beer trademarks but also many other alcoholic beverages, the differentiation and recognition of packaging is of great importance as well.

The flavor stability is one of the biggest shelf-life concerns in the beer. The beer has complex soft taste and flavor although, according to the sensory specifications, shows low flavor stability compared to other alcohol beverages. In general, beer aging results in decreased bitter taste, increased sweet taste and increased caramel, ribes and toffee-like aromas. Beer in PET bottles is much more exposed to external influences and the quality of the beer in this type of packaging is unstable comparable to beer in glass bottle, cans and kegs.

Visual and sensory characteristics of lager beer in PET were studied in period of 3 months in order to estimate whether drastic changes in these characteristics will occur. The HS-GC and sensory analysis of beer in PET were made weekly, in a period of 3 months, to follow the beer compounds changes that cause the formation of off-flavours. Sensory changes are good indicator for shelf-life prediction of beer in PET packages.

It is generally recognized that the staling of bottled beer is very complex because of the thousands off-flavor-active compounds included. From the performed research, it is obvious that beer in PET loses its sensory quality even in the first weeks of packaging. Oxidative produced unsaturated carbonyl compounds play a major role in the development of stale flavor in a beer packed in PET. Beside the fact that beer in PET package becomes mainstream in South-West Europe countries, especially for economic beer brands, still the glass bottles remain irreplaceable package.

Key words: beer aging, PET packaging, flavor stability, HS-gas chromatography, sensory evaluation

## BFP-44

### RELATION OF DIFFERENT CONCENTRATIONS OF *ALLIUM FLAVUM* BULB EXTRACT AND ITS ANTIOXIDANT CHARACTERISTICS

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Antioxidants play essential role in blocking free radicals production processes and oxidative stress, and in that way they are considered as crucial factors in prevention and treatment of many diseases. *Allium flavum*, is a wild grown member of *Alliaceae* family. It is known that lots of species from genus *Allium* show some therapeutic effects and many of them were studied regarding their chemical composition and biological activity. *A. flavum* was not studied in detail. Because of possible antioxidant activity of this plant, a methanol extract of its bulb was evaluated, and a relation between antioxidant efficiency and different concentration of extract was established.

Antioxidant characteristics were estimated applying four different assays: total reducing power (TRP), 2,2-diphenyl-1-picrylhydrazil radical scavenging activity (DPPH), total polyphenol content according to Folin-Ciocalteu method and total flavonoid content. Activities of samples were expressed as equivalents of appropriate standards.

In case of DPPH antioxidant activity method, concentrations of studied extract were ranged from 0.01 mol dm<sup>-3</sup> to 1.00 mol dm<sup>-3</sup>, while for the other three methods, concentrations were ranged from 0.1 mol dm<sup>-3</sup> to 1 mol dm<sup>-3</sup>.

With increase concentrations, considering TRP and flavonoid content, antioxidant activity decreased, while in case of polyphenol content, reversed dependence was registered. According to DPPH method, saturation curve illustrating relation between antioxidant activity and extract concentrations was obtained.

Key words: antioxidant activity, *Allium flavum*, DPPH, polyphenols, flavonoids

**BFP-45**

**DISTRIBUTION OF IRON, ZINC, COPPER, CADMIUM AND LEAD IN  
*AEGOPODIUM PODAGRARIA*, *CHELIDONIUM MAJUS* AND *HYPERICUM  
PERFORATUM* FROM VIDLIC MOUNTAIN (SERBIA)**

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Plants absorb heavy metals from soil via root, but under certain conditions shoots (aerial parts) may be also involved and they can accumulate significant amounts of heavy metals, without noticeable signs of damage. When the concentrations of heavy metals exceed a critical limit, disturbances of the living processes in plants occur. The aim of this research work was to examine the consequences of wildfire on metal content in certain plants. The study was focused on five metals which are wide present in soil (Cd, Cu, Pb, Fe and Zn). Since, wildfires cause modification of soil organic substances and consequently of soil structure, the presence of metals was examined in plants from two different localities on Vidlic Mountain (Serbia): a region affected and a region not affected by wildfire.

Shoots and roots of the following plants were examined: *Aegopodium podagraria* (*Apiaceae*), *Chelidonium majus* (*Papaveraceae*), *Hypericum perforatum* (*Hypericaceae*). The plant samples were digested applying wet procedure, and metal concentrations were measured using ICP-OES.

Content of Fe was the highest in roots of *A. podagraria* (region affected by fire) while the concentration of Zn was the highest in roots of the same plant but from region not affected by wildfire. *H. perforatum*, shoots (not affected area) has the largest concentration of Cu, while *A. podagraria* and *H. perforatum* (roots, not affected area) contain the highest concentration of Cd. The content of Pb was the highest in *C. majus* (roots) from the area not affected by wildfire.

In most cases, the content of heavy metals was higher in plants that grew in the area not affected by wildfire.

Keywords: metal content, wildfire, *Aegopodium podagraria*, *Chelidonium majus*, *Hypericum perforatum*

**BFP-46**

**THE EFFECT OF PROPIONIC BACTERIA ON PHYSICO-CHEMICAL  
PROPERTIES OF HARD BEATEN CHEESE**

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Hard beaten cheese is an indigenous product to Macedonia, in particular to the region of Mariovo. Originally, it has been produced exclusively from unpasteurized sheep milk. However, this traditional product, as many other food products, has undergone some changes in the manufacture. It is now produced on a large scale, and from varieties of milk including a mixture of sheep and cow milk, pure cow milk and a mixture of sheep and goat milk. During this process, some of the characteristics of the hard beaten cheese were lost.

In this study, attempts have been made to modify the industrial production of beaten cheese so that its authentic quality and look are regained. In addition to starter culture, a second starter culture comprising of propionic bacteria was introduced. These bacteria are responsible for creating a specific flavor and characteristic holes in the cheese. The flavor results from the propionate, and the holes also known as "eyes" from bubbles of carbon dioxide. The appearance of holes in the traditionally manufactured beaten cheese was due to the microflora present in the fresh milk. With its pasteurization, the milk changed its physico-chemical composition and its microflora, which affected the aroma and the formation of "eyes" in the cheese.

The composition of cheese produced on industrial scale with and without propionic bacteria was followed during ripening. The cheeses were analyzed for dry matter, fat, protein, salt, pH, titratable acidity and soluble nitrogen in water, trichloroacetic acid and in phosphotungstic acid. The hard beaten cheese with propionic bacteria showed the desired texture, characteristic holes and aroma, and was well accepted by the consumers. This is a good basis for introducing a traditional quality to an industrially produced hard beaten cheese.

Key words: propionic bacteria, hard beaten cheese, traditional food.

**BFP-47**

**ANALYSIS OF PROTEIN SEQUENCE/STRUCTURE SIMILARITY OF  
PROTEASES**

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Multiple protein sequence alignment remains a central method for understanding the function of groups of related protein sequences. Proteins display diverse sequence/structure similarity relationships. Understanding protein similarity relationships is important for the annotation of genome sequences. Proteins with high sequence identity and high structural similarity have a tendency to possess functional resemblance and evolutionary relationships, yet examples of proteins deviating from this general relationship of sequence/structure/ function homology are well-recognized. For example, high sequence identity but low structure similarity can occur due to conformational flexibility, mutations, solvent effects, and ligand binding.

All calculations and analysis of the protein primary sequences were accomplished with **Jalview Version 2.7** a multiple sequence alignment editor and analysis workbench.

The goal of this presentation is to estimate the ability of the program to calculate some properties of the different protease such as pairwise alignment, multiple alignments, consensus conservation and clustering, and to identify the structure similarities that are conserved throughout a given protein family of proteins. In the analysis were encompassed several proteases clusters from Internet protein data bases such as PDB (<http://www.rcsb.org/>) and UNIPROT (<http://www.uniprot.org/>).

In addition, the tool for principal component analysis (PCA) and other software is used to calculate charges, different structure indices, pI etc.

Key words: proteases, multiple alignments, structure indices, protein structure indices

**BFP-48**

**COMPARAISON OF THE PROTEIN PRIMARY SEQUENCIES AND  
TRIDIMENSIONAL STRUCTURES OF THE CALMODULIN AND  
CALMODULIN LIKE PROTEINS**

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Multiple sequence alignment remains a crucial method for understanding the function of groups of related DNA and protein sequences. When we compare the sequences of proteins, we analyze the similarities and differences at the level of individual amino acids with the aim of deducing structural, functional, and evolutionary relationships among the sequences under study. The most common comparative method is sequence alignment, which offers an explicit mapping between the residues of two or more sequences. This study may involve mapping profiles of conformational preferences, accessibility, hydrophilicity/hydrophobicity, and so on. Different multiple sequence alignment programs and various scoring schemes have been used to analyze potential relationships among sequences.

All evaluation of the protein primary sequences were accomplished with **Jalview Version 2.7** a multiple sequence alignment editor and analysis workbench.

The aim of this work is to estimate the ability of the program to calculate some properties of the calmodulin and calmodulin like proteins such as pairwise alignment, multiple alignments, consensus conservation and clustering, and chemometrics methods and to identify the structure similarities that are conserved throughout a given protein family of different calmodulins and calmodulin like proteins. In the analysis were included several calmodulin and calmodulin like clusters from protein data bases such as PDB (<http://www.rcsb.org/>) and UNIPROT (<http://www.uniprot.org/>).

In addition, the tool for principal component analysis (PCA) of the protein sequences was used to describe the similarities of the protein sequences.

Comparison of the tridimensional structures with on line and off line software and the calculation of other properties of proteins are in progress.

Keywords: calmodulins, calmodulin like proteins, multiple alignments, principal component analysis (PCA)

## BFP-49

### ANALYSYS OF THE PROTEIN PRIMARY SEQUENCES OF AMYLASES

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Comparison of protein and nucleotide primary sequence information is rapidly becoming the major basis of data in the elucidation protein and DNA properties and the molecular mechanisms of replication and evolution of all organisms. There are principally several levels in the analysis of primary sequence information: (1) the search for homologues, (2) the multiple alignments of homologues, (3) the phylogenetic reconstruction of the evolutionary history of homologues and (4) sequence structure correlations.

Many multiple sequence alignment programs and various scoring schemes have been developed to analyze potential relationships among sequences.

In this work all comparison of the sequence were carried out with Jalview program **Jalview Version 2.7-a** multiple sequence alignment editor and analysis workbench.

The goal of this analysis is to estimate the ability of the software to calculate some properties of the proteins such as pairwise alignment, multiple alignments, consensus conservation and clustering, PCA analysis etc. and to identify the ordered series of motifs that are conserved throughout a given protein family of different amylases. In the analysis were included 26 amylases clusters and their sequences and structures from several protein data bases such as Protein Data Bank (<http://www.rcsb.org/>) and UNIPROT (<http://www.uniprot.org/>).

Keywords: protein, amylase, multiple alignments, protein motifs and Jalview program

## BFP-50

### PHENOLIC CONTENT OF VRANEC GRAPES DURING RIPENING

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Grape polyphenols are characterized by a large range of structures diversely distributed in every part of the berry. The knowledge on the phenolic composition of grapes and its evolution during ripening is thus of crucial importance in relation to wine quality. Among them, anthocyanins, located in the skins, are responsible for the red colour of the grapes, while flavonoids and especially flavan-3-ols intervene in their taste, astringency and bitterness. In this study, total polyphenols, flavonoids, flavan-3-ols and anthocyanins were determined in the pulp, skins and seeds of Vranec grapes in three ripening stages: veraison, technological and physiological ripeness, applying standardized spectrophotometric methods. Extraction of phenolic compounds from grape pulp, seeds and skins was performed with acetone/water mixture (80/20, v/v). Results showed that the concentration of total phenolics in skins increased during ripening (21.21 mg/g, 48.17 mg/g, 61.55 mg/g, at the beginning of the ripeness, at technological and physiological ripeness, respectively), but they slightly decreased in the seeds. Concentration of the total flavonoids in skins and seeds increased during the ripening process, as well as the anthocyanin content in skins, which was the highest in the late harvested grapes. Flavan-3-ols in the seeds were present in highest concentration at the veraison phase, while in the skins their content increased during ripening reaching the highest amount at the technological stage. Vranec grapes presented high content of phenolics, flavonoids, anthocyanins and flavan-3-ols, which are main antioxidant components in the wines. This traditional domestic variety, rich in polyphenols and colour, dominates in the Macedonian vineyards and possesses a strong capacity for making a high quality wine recognizable in the world.

Keywords: Vranec variety, grapes, total phenolics, flavonoids, flavan-3-ols, anthocyanins, ripening.

**BFP-51**

## **QUALITY CHARACTERISTICS OF THE WHEAT VARIETIES FROM PELAGONIJA REGION**

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The quality characteristics of wheat as a raw material in the milling process are the most important for production of high quality flour. Wheat varieties with superior quality attributes are highly desired as they can better satisfy the requirements of the market. The wheat variety and the region where it grows are highly influencing factors affecting the quality of wheat. Also, the wheat classification in silo bins is performed according to these two criteria, its variety and quality.

In the industrial laboratories, the quality wheat characteristics are commonly determined by the rheological methods using extensograph and amylograph. Currently, in the determination of wheat quality characteristics a new method and equipment, consisting of a mixolab device, is used.

This study was aimed to evaluate the quality of wheat varieties of the species *Triticum aestivum* L. from Pelagonija region. The investigated wheat varieties Altana, EMS and Pobeda were collected in 2011 from the region Ergela, Radobor, Novaci and Porodin. Rheological parameters were determined using Brabender extensograph and amylograph, and Chopin mixolab.

The obtained results showed that the best rheological characteristics and high quality was determined in the Altana wheat variety produced in the Novaci region. It was characterized with high extensograph energy of 148 cm<sup>2</sup>, 1000 AE maximal viscosity and mixolab index 3-58-889.

Key words: wheat, characteristics, flour, quality characteristics, energy, mixolab index

## BFP-52

# EFFECT OF PACKAGING AND LIGHTING ON CHANGES IN APPEARANCE, TASTE, ODOR AND NUTRITIVE VALUE OF FULL FAT PASTEURIZED MILK DURING STORAGE

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Dairy products are often exposed to light during retail storage and display, although it is well known that light initiate oxidative processes which caused diminishing of nutritive value, discoloration and development of off flavors in food. These changes are especially marked when products are packed in transparent containers. In our country we can found milk packaged in different packaging. In the markets it is usually placed in refrigerators lightened with fluorescent lamps. The objective of this study was to determine changes in sensory and biochemical characteristics of full fat pasteurized milk packaged in bottles with different light barrier, during storage in refrigerator (7°C) in dark and exposed to fluorescent light. Two samples of milk, one packaged in transparent PET, and the other in Tetra pack were purchased from local market. Their appearance, taste, odor and content of riboflavin, vitamin A, thiamine and Maillard-products were assessed immediately after delivering from the producers and after 2, 3 and 7 days of adequate storage. Colorimetric indices  $L^*$ ,  $a^*$ , and  $b^*$  were used to confirm their appearance, sensory descriptive test to evaluate taste and odor and fluorescent spectra to follow biochemical changes. The results demonstrate very similar and minor changes in quality parameters during storage of both milks in dark. However, more evident were light induced changes in the milk packaged in transparent PET.

Key words: pasteurized milk, light induced changes

**BFP-53**

**ANTIMICROBIAL BEESWAX EDIBLE COATINGS WITH MONOLAURIN IN  
PRESERVATION OF FRUITS AND VEGETABLES**

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Edible films and coatings have been extensively used in food industry. Nowadays, their characteristics become more and more sophisticated and their potential applications are extensively broadened. Prevention of product deterioration, minimization of packaging manipulation, prolongation of the product shelf life and protection of the environment are the most common motives for a research that refers to edible coatings issue. Incorporation of different nutraceuticals or antimicrobial agents gives the edible coatings another perspective: they have an additional active packaging function.

In this work the possibilities for utilization of beeswax edible coatings on different fruit and vegetable products have been investigated. Monolaurin, the food grade emulsifier, was used as a multifunctional agent: as a coating softening agent and as an antimicrobial agent. Beeswax based edible coatings containing monolaurin were applied on fresh cuts, whole fresh fruits and vegetables and processed fruits and vegetables. The effect of edible coatings on the deterioration prevention and prolongation of the product shelf life was investigated. The preservation effect of the monolaurin was studied in detail. Its antimicrobial activity was compared with the activities of some most commonly used preservatives, such as the benzoic and the citric acid. Thus, the antimicrobial activity of monolaurin against the yeast *Saccharomyces cerevisiae* was studied. The MIC value for this microorganism was 1000 mg/L. The total cell counts of the products coated with monolaurin based coatings and infected by *S. cerevisiae* were several orders of magnitude lower than that of the non coated infected products.

Key words: Beeswax edible coatings, monolaurin, antimicrobial, preservation, fruits and vegetables

**BFP-54**

**DETERMINATION OF AFLATOXIN B1  
AND G1 IN GRAIN FOODS**

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Aflatoxins are potentially toxic, carcinogenic, mutagenic, immunosuppressive agents, produced as secondary metabolites (such as the group of difuranocoumarins) by different fungi. *Aspergillus flavus* and *Aspergillus parasiticus* under favorable conditions of temperature and humidity grow on certain foods and feeds and produce aflatoxins. Among the 18 different types of aflatoxins, the major members are the aflatoxins B1, B2, G1 and G2. The most pronounced contamination has been encountered in nuts, peanuts, and other oilseeds, including corn and cottonseed.

In this study a rapid and easy luminometric method (Charm Science) and the classic thin layer chromatography method were used for determination of aflatoxins B1 and G1 in 25 samples of grain foods such as: almonds, hazelnuts, walnuts, chickpeas, peanuts, coconuts, sesame seeds, pumpkin seeds and coffee.

After validation of the methods and after determination of aflatoxins B1 and G1 in different grain foods, higher level of aflatoxin B1 was found in 20% of the samples. The contents of aflatoxin B1 was higher than permitted value (3µg/kg) in four samples of peanuts and one hazelnut sample. Aflatoxin G1 was higher in two samples of peanuts and one sample of hazelnut. These results confirm that aflatoxin B1 is predominant over aflatoxin G1 in a variety of foods with high fat content.

The examinations also showed that the accuracy of the rapid Charm luminometric method for aflatoxin determination was slightly more sensitive than the classical thin layer chromatography method. Higher value of determined aflatoxins B1, which is the most toxic, indicated that more food quality controls for mycotoxins are needed.

Key words: aflatoxins, grain foods, Charm luminometric method, TLC method

**BFP-55**

**THE EFFECT OF RAW MATERIALS AND FERMENTATION CONDITIONS  
ON FLAVONOIDS CONTENT OF GRAPE BEER**

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Over the last decades, there has been an increased interest in researching the potential health benefits of moderate wine and beer consumption. Researches indicate that wine and beer consumed moderately can have a very favorable effect on overall health condition. The effect can be explained by a high content of antioxidants and other biologically active compounds, particularly flavonoids which can prevent occurrence of some diseases, especially cardiovascular disease. In this research, a special type of beer, the grape beer, was produced using three different grape varieties Prokupac, Pinot Noir and Cabernet Sauvignon. Beer samples were fermented using conventional brewer's wort and 20 % and 30 % of grape mash. The fermentation was carried out using two different yeasts: *Saccharomyces pastorianus* industrial strain obtained from one of the Serbian breweries and wine yeast *Saccharomyces cerevisiae* K1-V1116. The influence of grape variety, proportion of grape and yeast strains on the flavonoids content was examined. The flavonoids content was determined according to the official EBC (European Brewery Convention) spectrophotometric method. The results suggested that grape varieties, their contents, as well as yeast strains had a very significant influence on the flavonoids content of obtained grape beers. The flavonoids content rang in samples went from 20.9 mg/L in beer without grape fermented by brewing yeast and up to 73.5 mg/L in beer with 30 % of Cabernet Sauvignon grape fermented by wine yeast.

Key words: beer, grape, flavonoids, fermentation

**BFP-56**

**THE INFLUENCE OF PRODUCTION PROCESS ON THE ANTIOXIDANT CAPACITY AND SENSORY CHARACTERISTICS OF HONEY LIQUER**

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Liqueurs are attractive beverage with pleasant sweet aroma and potential bioactive compounds which derived from the raw material of product. Recent years, the liqueurs with the honey as sweetener and the extract of herbs as flavor base are very interesting products in Serbian markets. The herbs and honey are rich source of aromatic compounds, but also it contains polyphenols, which improve the functional properties of these beverages. The technological problem in production of this beverage is the fact that the honey causes the turbidity, but filtration process affects on the content of bioactive compounds.

In this study it was investigated the influence of filtration process on the total polyphenols content, antioxidant activity and sensory characteristics of special liquers. The total phenolic content of liqueur samples was determined according to the Folin-Ciocalteu spectrophotometric method. The total antioxidant capacity was evaluated using DPPH and FRAP methods. Sensory characteristics of the liqueurs were determined using modified Buxbaum model of positive ranking. The common quality parameters were evaluated: clearness, color, distinction, odor and taste. In this evaluation a brandy sample may have a maximal score of 20 points.

Among the studied samples, the significantly higher content of polyphenols had the unfiltered sample. The total phenol content (TPC) of unfiltered samples was 158.6 mg/L, while the TPC of filtered sample was 109.78 gallic acid equivalents. The antioxidant capacity of unfiltered sample was 0.61 and 0.41 mM Trolox for filtered sample according to DPPH assay, and 0.961 and 0.61 FRAP units, respectively according to FRAP method. Also, the sensory characteristics of unfiltered sample was the best rated. The obtained results showed that the process of filtration adverse affect on the healthy properties and sensory characteristics of honey liqueurs.

Keywords: liqueur, filtration, polyphenols, antioxidant capacity, sensory characteristics

## BFP-57

### STUDY OF ENZYMES IMPACT ON BEER FILTERABILITY

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The aim of this paper is to provide information for identification of potential critical parameters of some Albanian beers that have a significant impact on optimization of filtration process. The processes prior to filtration indeed have a significant impact on solids loading on a beer filter. The best practice for filtration optimization process is to control the suspended particulates (yeast, haze) at every stage of beer chain production. There are several improvements of processes that can be used to reduce solids loading in the beer, e.g., settlement by gravity or centrifugation (or combination of them), extended lagering periods, addition of enzymes, flocculants and clarifiers to reduce both, yeast and haze loadings. It has been under our responsibility to study selection and combining of some elementary procedures and entire processes, in order to take an optimal beer consistency that will lead to an optimal filtration process.

After experimental works and results analysis, it has been verified that yeast and proteins dominate in the filter cake after the filtration process, but if we introduce filter-aids and centrifugation, then carbohydrates will dominate in the filter cake.

More important carbohydrates include: unmodified starch, dextrin, pentosans, and  $\beta$ -glucans. Carbohydrates that have a significant impact on filtration were tested using enzymatic techniques for three different beers. The filterability of a beer was represented by the maximal filtrate volume,  $V_{\max}$  in a given differential pressure.

**Key words:** Filtration process, stabilization, haze, yeast, enzymes, filter-aids.



**BFP-59**

**OPTIMIZATION AND METHOD VALIDATION FOR ASSAY  
DETERMINATION OF DOXYCYCLINE, OXYTETRACYCLINE AND  
TETRACYCLINE IN PHARMACEUTICAL PRODUCT**

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Tetracyclines are broad spectrum antibiotics and very commonly used to treat acne and skin infections; systemically for infections of the respiratory, urinary and gastrointestinal tract.

A method for assay determination of doxycycline (DOX), tetracycline (TC) and oxytetracycline (OTC) respectively in a final pharmaceutical product was optimized and validated. Extraction with several mediums such as water, ethanol, methanol and 0.1M HCl, was tested. The water was chosen as solvent because of its availability; it is more ecological and cheaper solvent.

Sample treatment involves simple extraction with the solvent, ultrasonic treatment and suitable dilution after filtration. The assay was determined UV-spectroscopically, with a *VARIAN Carry Win 50* UV/Visible spectrophotometer, in a 1-cm cell at wavelength range 190 - 500 nm, with resolution 0.5 nm and scan rate of 300 nm/min.

Each method was validated according to the ICH quality guidelines, *i.e.* the guideline for Validation of Analytical Procedures Q2 (R1). All the tested parameters were within the tolerated limits for assay determination, from 98% to 102%. The LOD of 0.4 µg/ml (DOX), 0.8 µg/ml (TC) and 0.57 µg/ml (OTC) and LOQ of 1.3 µg/ml; 2.4 µg/ml and 1.68 µg/ml, respectively, were calculated. A high linear correlation between the obtained detector signal is confirmed with high correlation coefficient of 0.9995 (DOX); 0.9997 (TC) and 0.9996 (OTC) expressed as average values of the measured absorbances of the standard solutions of DOX, TC and OTC in the range from 0.7 – 15 µg / ml; 0.4 - 60 µg / ml and 0.8 – 40 µg / ml, respectively. Recovery was shown to be good in all cases, ranging from 98.08 to 101.67 %, which excludes the possibility of interference of the components of placebo with the absorbance curve of each of the tetracycline and the accuracy of the method is confirmed. For determination of the precision of the method, the assay test was performed ten times, preparing separate test solutions using same homogeneous sample expressed as RSD with value of 1.53% for DOX; 3.53% for TC and 3.85% for OTC.

The presented methods offer the simplicity needed testing a large numbers of samples in a short period of time, necessary for routine analyses. The tested specimens include: DOKSICIKLIN caps. 100 mg; MEDOCYCLINE caps. 100 mg; NEOSULFOX P oral powder; and GEOMYCIN soluble powder.

Keywords: assay, validation, UV spectrophotometry, Doxycycline, Tetracycline, Oxytetracycline

**ELECTROCHEMISTRY (EL)**

**EL - 1****STRUCTURAL INVESTIGATION OF PTM-MO<sub>x</sub> COMPOSITE CATALYSTS**

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Our research in the last years is focused on the synthesis of different combinations of mono- and bimetallic Pt compounds, oxides and composite materials and their application as catalysts for oxygen evolution reaction (OER) in PEM water electrolysis. The supporting material of choice is Magneli phases titania (trade name Ebonex) known for its stable behavior and good corrosion resistance at the high anodic potentials of intensive oxygen evolution. In addition, it contributes to the efficiency of the composite catalyst via electronic interactions with the metallic components.

This work summarizes results on the structural characterization of series Pt-based catalysts prepared by wet sol-gel method using appropriate ratios between Pt- acetylacetonate  $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$  and M-acetylacetonate  $(\text{M}[(\text{C}_5\text{H}_7\text{O}_2)_n]_m, \text{M} = \text{Ni}, \text{Fe}, \text{Co}, \text{Mn}, \text{Cr})$  precursors, co-deposited on mechanically activated Ebonex. The structure and composition of the synthesized composites are studied by X-ray diffraction (XRD) and X-ray-photoelectron spectroscopy (XPS). Two types of catalysts are obtained - Pt-M/Ebonex and Pt-MO<sub>x</sub>/Ebonex, depending on the electronic structure of the alloying metal. For metals with hyper-d-electron character (Fe, Co, Ni) a formation of Pt-M alloy type solid solution is registered. The alloying is accompanied by decrease in the lattice parameter and the crystallite size. In contrast, when M is a hypo-d-electron element (Cr, Mn) then Pt-MO<sub>x</sub>/Ebonex is obtained. Nevertheless, the established differences in the composition, both types of bimetallic catalysts demonstrate enhanced efficiency toward oxygen evolution reaction compared to pure Pt/Ebonex. For Pt-MO<sub>x</sub>/Ebonex type, the increased activity is related to hypo-hyper-d-interelectronic bonding interactions between the platinum and MO<sub>x</sub>, while for PtM/Ebonex type, the size effects are predominant.

Key words: PEM water electrolysis; Ebonex; PtM-MO<sub>x</sub> composite catalysts; XRD; XPS

## EL - 2

**THE NEW H<sub>2</sub>O<sub>2</sub> SENSORS BASED ON SILVER NANOWIRE ARRAYS**M. Jarosz<sup>1</sup>, A. Brzózka<sup>2</sup>, G. Sulka<sup>1</sup>, M. Jaskuła<sup>1</sup>

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The hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), as a strong oxidizer, has a wide range of applications. For instance, H<sub>2</sub>O<sub>2</sub> is used in cosmetic and pharmaceutical production, sterilization, organic synthesis and clinical applications. Furthermore, it is produced by immune system cells in the human body. Thus, an effective method of H<sub>2</sub>O<sub>2</sub> detection has been a significant challenge, especially when it comes to sensors. A great number of methods, both analytical and non-analytical, such as chemiluminescence, titrimetry, spectrophotometry, have been developed to detect H<sub>2</sub>O<sub>2</sub>. Among them, the electrochemical detection appears to be the most preferable. Its high efficiency and sensitivity along with the operational simplicity at a relatively low cost, allowed us to apply it for an accurate H<sub>2</sub>O<sub>2</sub> detection. Those sensors detect H<sub>2</sub>O<sub>2</sub> at a high potential, which brings a problem of interferences in biological samples from other oxidizable compounds, e.g. ascorbic acid (AA), acetaminophen (AAP), uric acid (UA). Therefore, developing a sensor for H<sub>2</sub>O<sub>2</sub> detection at a lower potential is of great importance.

To modify electrodes, various materials such as enzymes, carbon nanotubes or macrocyclic complex of transition metals have been used. Due to their distinctive properties, like unique catalytic and optical properties and high surface to volume ratio, nanomaterials play an important role in constructing novel electrodes for sensing applications. Silver nanowires and nanotubes, among other noble nanomaterials, have engendered interest in recent years. Biocompatibility and low toxicity, along with bactericidal properties make silver nanomaterials very promising components for future electrochemical sensors.

In this research we used Ag nanowire arrays that were obtained by DC electrodeposition of silver in porous anodic aluminum oxide (AAO) templates having different diameters. The AAO templates were prepared by two-step anodization of aluminum in acid solution. The Ag nanowire arrays were used to study an electrocatalytic reduction of H<sub>2</sub>O<sub>2</sub> in a 0.01 M phosphate buffer solution of pH 7.4. The cyclic voltammograms showed that the H<sub>2</sub>O<sub>2</sub> reduction starts at low potential (-0.4 V vs. SCE) and that the response to different H<sub>2</sub>O<sub>2</sub> concentrations is rapid. The approach of using silver nanowires as H<sub>2</sub>O<sub>2</sub> sensor has proved to be very promising.

Key words: hydrogen peroxide sensor, silver nanowire

## EL-3

## HYDROGEN SENSING BEHAVIOUR OF TELLURIUM THIN FILMS STUDIED BY A.C. MEASUREMENTS

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The hydrogen gas sensing performance of microcrystalline tellurium thin films were investigated by method of impedance spectroscopy. For the first time it is pointed out that tellurium films exhibit sensitivity to H<sub>2</sub> at room temperature along with sensitivity to NO<sub>2</sub>. Tellurium films of  $\approx 100nm$  thickness were prepared by thermal vacuum evaporation of pure tellurium onto ceramic substrates with priorly deposited platinum interdigital electrodes. Exposure to hydrogen gas resulted in changes in the impedance of the film. Analyses in complex interpretation allowed evaluating the characteristic frequency, time constant, resistance and capacity of the film in different target gases, including hydrogen. Estimated values of impedance, time constant,  $R_{\omega}$  and  $C_{\omega}$  of the film at characteristic frequency  $f_m$ , in different environments are:

Environment	$f_m$ (kHz)	$Z$ (kOhm)	$\tau_m \cdot 10^{-7} s$	$R_{\omega}$ (kOhm)	$C_{\omega}$ (pF)
Dry air	900	13,3	1,8	19,2	9,6
H <sub>2</sub> 1% by vol.	600	19,8	2,7	31,7	8,5
1,5 ppm NO <sub>2</sub>	1500	7,5	1,1	11,8	9,3

It is shown that impedance spectra are strongly influenced by gaseous environment but the effect of target gas is mainly due to variation of resistance of the film. The aging noticeably influences the resistance of the film only at high (>500 kHz) frequencies, but the capacity diminishes with aging more then twice through whole spectrum. In contrast to the effect of aging, heating influences only the resistance of the film. Elemental hydrogen occurs only as diatomic gas molecules at normal conditions. Perhaps, the sensitivity of tellurium films to H<sub>2</sub> arises because of the reducing effect of oxygen priorly absorbed on the surface of the film from carrier (dry air) gas. The high concentration of oxygen in carrier gas promotes the formation of a catalytic gate, which can be removed by other gases. Assuming that molecular hydrogen removes the priority-adsorbed oxygen we can expect the decrease of both, hole concentration and conductivity of the surface and intragrain regions of tellurium film. Due to impedance change in different direction, reducing H<sub>2</sub> may be distinguished from oxidizing NO<sub>2</sub>, hence the effective, operating at room temperature H<sub>2</sub> sensors can be manufactured using tellurium-based films.

Keywords: Gas sensing, Tellurium, Hydrogen

## EL-4

# CORROSION CONTROL AND MANAGEMENT IN OKTA CRUDE OIL REFINERY

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Corrosion is a major concern in petroleum refining and petrochemical operations. The corrosive deterioration is the main cause for the equipment and piping breakdown and failure. Additionally, it reduces the efficiency of the process and increases the operating and maintenance costs significantly. Due to the extremely hazardous nature of the fluids and gases processed in refineries, the safety and well being of both plant employees and the public are put at risk by corrosion. Equipment failures could result in severe damage to entire process units, as well as the environment. For these reasons, the corrosion monitoring and management is an essential aspect of the management of every petroleum refinery.

The main responsibility of the Technical Inspection Department in OKTA Crude Oil Refinery is the detection, inspection and corrosion protection of the refinery equipment and piping. The subject of this paper is the analysis of the main causes for corrosion and the most common types of corrosion present in OKTA, as well as the corrosion management and control. The detection and inspection of equipment deterioration due to corrosion is primarily done by visual inspection. The state of the metal material is inspected with ultrasonic method, thickness measurement and defectoscopy, and hardness measurement. The equipment subjected to high-temperature conditions is inspected with IR camera. The inspection reports are stored in the Technical Inspection Department database and are used for equipment analysis, corrosion rate determination, remaining life calculations and fitness for service.

Keywords: refinery, corrosion, inspection, corrosion management

## EL-5

# INFLUENCE OF PARTICLE SIZE ON ELECTRICAL CONDUCTIVITY OF BIODEGRADABLE COPPER AND LIGNOCELLULOSE BASED COMPOSITES

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This article is concerned with the investigation of influence of particle size of the basic components: electrodeposited copper powder and lignocellulose (LC) as well as composite materials prepared by the compression molding of LC and galvanostatically obtained copper powder mixtures, on the electrical conductivity of composites. Analysis of the most significant properties of individual components and prepared composites included quantitative structural analysis, morphological analysis, determination of density and porosity and measurements of electrical conductivity. Different investigation techniques including SEM, TGA, DSC, X-ray, FTIR, particle size distribution and conductivity measurements were used.

Results have shown that the powder has very high surface area and it has pronounced dendrite branching with well-developed primary and secondary dendrite arms. The conductivity measurements have been conducted on all the samples and have showed S-shaped dependency with percolation transition from non-conductive to conductive region, typical for such polymer composite materials. The electrical conductivity of all particle size composites with particle size is  $< 10\text{-}15$  MS/m, unless the metal content reaches the percolation threshold of 14.4% (v/v) for composites with particle size  $< 88$   $\mu\text{m}$ , beyond which the conductivity increases markedly by as much as 14 orders of magnitude. The pressure does not play significant role on the percolation threshold with this particle size. However, by lowering the particle size, the influence of the composite formation pressure increases. The percolation threshold is lowered from 2% (v/v) Cu for 10 MPa up to 5.3% (v/v) Cu for 27 MPa for composites with particle size  $< 45$   $\mu\text{m}$ . It was found that this transition occurs at lower volume fractions than stated in the literature, which can be due to the filler with high specific area. This research has undoubtedly shown that galvanostatically obtained copper powder plays significant role with its indented area in formation of greater number of contacts with smaller volume fractions. In this manner the value of percolation threshold is lowered and this is amplified more by lowering the particle size.

Key words: Conducting polymer composites, electrolytic copper powder, electrical conductivity, percolation threshold, lignocellulose

## EL-6

# APPEARANCE, CONTROL AND PREVENTION OF CORROSION IN THE BREWING INDUSTRY

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In the food industry, the brewing sector holds a strategic economic position, being the most consumed alcoholic beverage, with the annual world beer production exceeding 1.85 billion hectolitres in 2010. In many regards breweries are unique in the food industry. In the food industry, the brewing sector is the one of the most severely affected by corrosion. The entire process uses large quantities of water for beer production, bottling, storage, as well as cleaning. The beer itself, as the main product in the process, is an acidic liquid, which is aggressive to low carbon steel and also contains live microorganisms, which can cause biofouling and biocorrosion. Also, the disinfectants and cleaning agents used in the plant are known to cause corrosion problems.

The corrosion in the brewing industry brings about significant expenses, in terms of repairing and replacement of equipment. Furthermore, the corrosion products dissolved in the beer can affect its quality. This work deals with the appearance of corrosion in different stages of the brewing process and auxiliary operations, as well as with the methods of management and prevention of corrosion. Different types of materials used in the brewing industry will be analyzed, regarding their corrosion resistance. Also, the conditions of the whole process which may cause corrosion will be considered. The corrosion control and prevention will be reviewed through controlling the process parameters, as well as selection of improved and alternative equipment materials.

Keywords: brewing industry, corrosion, causes and solutions

## EL-7

### COMPLEXATION OF ZINC(II) IONS WITH NITRILOTRIACETIC ACID IN PRESENCE OF GLUTARIC ACID

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The object of this study was polarographic investigation of the interaction of Zn(II) ion with complexation agent nitrilotriacetic acid (NTA) in the presence of glutaric acid at concentrations of 0.1 and 0.01 mol/dm<sup>3</sup> at two pH values (pH=4 and pH=6). Same measurements were done with perchlorates, which were used as comparing standard. It is well known that perchlorates are inert ligands for complexation.

The investigation was conducted with differential pulse polarography (DPP). The working Zn(II) ion concentration was 2x10<sup>-4</sup> mol/dm<sup>3</sup>. That solution of Zn(II) was titrated with NTA complexing agent in concentrations from 2x10<sup>-5</sup> to 2x10<sup>-3</sup> mol/dm<sup>3</sup>.

From the obtained experimental results gained from the polarographic wave, it was concluded that glutarate ions like complexation agents with Zn(II) give no well-defined wave, but they coexist with Zn(II)ion wave. However, we have an avoidance of potential of half-polarographic wave towards negative values. During the titration of Zn(II) ion with NTA, in perchlorates, as well as in glutaric acid it has been noticed the formation of stable complex Zn(II)NTA, which appeared in the defined potential -1500 mV towards referent electrode Ag/AgCl. Experimental measurements confirm that in order to achieve the same extent of complexation of Zn(II) ion, it is necessary to use largerer NTA quantity under the same conditions in glutarate solution than in perchlorate solutions. This is due to the formation of labile Zn(II)glutarates complexes in glutarate solutions, which happen to be in competition with the stable Zn(II)NTA complex.

Key words: Zinc(II) ions, nitrilotriacetic acid, complexation, differential pulse polarography, Zn(II)NTA complex

## EL-8

### THE INFLUENCE OF THE NANODIAMOND PARTICLES IN THE PROCESS OF ELECTROCHEMICAL CHROME PLATING

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The electrochemical chromium coatings on steel give a nice outside appearance of the products, increase the hardness and the wear resistance of the basic material. The modification of the chromium galvanic coatings with nanodiamond particles additionally improves these properties.

The influence of the current density, duration of the galvanization and the concentration of the nanodiamond particles in the electrolyte on the characteristics of the coatings: chromium yield, thickness and microstructure, as well as on their properties – microhardness and wear resistance were studied.

The microhardness and the wear resistance are increased with the increase of the content of the nanodiamond particles in the electrolyte. At concentration 42 g/l they are respectively 9 and 6 times larger than the microhardness and the wear resistance of the steel.

Original data of the behavior and the role of the nanodiamond particles in the process of electrochemical deposition of chromium are obtained. This data gives insight into the mechanism of its action.

Key words: electrochemical chrome plating, nanodiamond particles, wear resistance

## EL-9

# POSSIBILITY OF APPLICATION OF GREEN INHIBITOR FOR THE PROTECTION OF COPPER

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The paper presents the assessment of copper corrosion protection by treatment of the corrosion surrounding with inhibitors. Copper samples measuring 50x50x1mm after chemical preparation were subjected to corrosion in uninhibited and inhibited solutions during time of 2, 4, 6 and 24 hours. Two basic solutions were used: 3% NaCl and 4% HCl. 0.1% solutions of thiocarbamide, furfural and hydrazine, and 1g/dm<sup>3</sup>, 2g/dm<sup>3</sup> and 3g/dm<sup>3</sup> of vitamin C and caffeine solutions were used as inhibitors.

Mean protection factor (z) in 4% HCl solution, with hydrazine as inhibitor, was 55.29%, while it was 64.12% and 76.84% with thiocarbamide and furfural, respectively.

Caffeine did not emerge as a good copper corrosion inhibitor. The degree of protection in both used solution varied in the range of 36-53%. If the market value of caffeine and achieved level of protection is taken into account, caffeine proves inadequate inhibitor for copper corrosion protection.

Vitamin C, as a green copper corrosion inhibitor, shows a different protective properties in the NaCl and HCl solutions. Medium level of protection in NaCl solution varies in the interval from 62.66% at a concentration of 1g/dm<sup>3</sup> of vitamin C, to 66% at a concentration of 3g/dm<sup>3</sup> of vitamin C. Medium level of protection in the HCl solution is also increased with increasing concentrations of vitamin C in solution, but it is much smaller than in NaCl solution, and it was in range from 42.44 to 61.93%. The degree of protection of vitamin C is the highest during 2 hours at a concentration of vitamin C of 3g/dm<sup>3</sup> used in both solutions. In 4% HCl after two hours the degree of protection was 67.17%, while in 3% NaCl level of protection was slightly higher, 68.71%.

Thus the highest protection effect was shown by furfural, but also vitamin C for 2 h. Vitamin C emerges as an inhibitor of the future, if its non-toxic nature and good protective properties are taken into consideration.

**Key words:** copper, inhibitor, corrosion, corrosion indicators, protective factor z.

## EL-10

### DEVELOPMENT OF ANODIC STRIPPING VOLTAMMETRIC METHOD FOR HEAVY METAL DETECTION AT BISMUTH-FILM ELECTRODES

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Anodic stripping method was developed for simultaneous determination of Pb(II), Cd(II) and Zn(II) by square-wave voltammetry (SWASV) using bismuth film electrode. This electrode type displays a well-defined, undistorted, highly reproducible response and a favorable signal-to-noise ratio. Anodic stripping voltammetry (ASV) is recognized as one of the most powerful tools in trace and ultratrace analysis of metal ions because it provides a wide linear dynamic range, low detection limit, and multi-element analysis capability. The bismuth film have been in situ prepared on a graphite substrate in 0.1 mol L<sup>-1</sup> acetate buffer solution (pH 4.6) containing 20 μmol L<sup>-1</sup> Bi<sup>3+</sup>(aq) ions, as well as the ions of the studied metals. The limits of detection were obtained at concentrations as low as 70 nmol L<sup>-1</sup> for Pb(II), 80 nmol L<sup>-1</sup> for Cd(II) and 0.1 μmol L<sup>-1</sup> for Zn(II) for 420 s deposition time without stirring. The proposed method was applied to the determination of Pb(II), Cd(II) and Zn(II) in river water samples.

Keywords: bismuth film electrode, anodic stripping voltammetry, heavy metals, ultratrace analysis

## EL-11

## PITTING CORROSION BEHAVIORS OF NIOBIUM AND TITANIUM

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Pitting experiments generally have been performed to predict pitting and crevice corrosion of the investigated metal in given electrolytic solution

In this work, using cyclic voltammetry and metallographic microscopy the pitting corrosion behaviors of niobium and titanium in strong mineral acids and hydroxides were investigated. The measurements were performed on the mechanically polished and electrochemically polished metal surfaces, as well as anodically oxidized at various voltages. For these measurements it was necessary to apply a slow potential scan in anodic direction beginning from OCP (open circuit potential) until a large increase of current in the active region occurs. When a forward scan reaches a pre-programmed current, usually near the maximum value in an active region, it reverses and begins the backward scanning in cathodic direction. The final pre-programmed potential scan should be more cathodic than the protection potential, *E<sub>pro</sub>*. The protection potential is the potential where the I-E loop closes in the reverse scan. Below it neither pitting nor crevice corrosion occur.

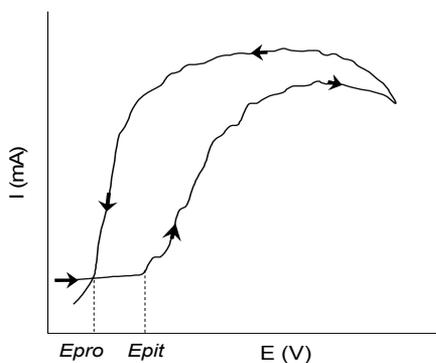


Fig.1. Simulated voltammogram of pitting corrosion on the metal-solution system

In fig.1 the simulated voltammogram of the metal solution system with existing pitting corrosion is given. The reverse scan is at a higher current level than the forward scan. The potential at which the current sharply increases is defined as the pitting potential *E<sub>pit</sub>*. When pitting occurs on the forward scan, the reverse backward scan will trace the hysteresis loop. The trace of the pitting loop is not continuous; it is rough, indicating pitting tendency. If the loop is larger, the tendency to pit is greater. If *E<sub>pit</sub>* = *E<sub>pro</sub>* there will be a small tendency to pit. If *E<sub>pro</sub>* is more positive than *E<sub>pit</sub>*, there will be no tendency to pit. If *E<sub>pro</sub>* is more cathodic than *E<sub>pit</sub>*, pitting will occur.

Our investigations have shown that the pitting tendency for both Nb and Ti are smaller in concentrated acid than in concentrated hydroxide solutions. Beside, the electro-polished metal surfaces are more resistant than mechanically polished ones.

Keywords: Pitting corrosion, titanium, niobium

**EL-12****COMPOSITE NON-NOBLE CATALYSTS FOR OXYGEN REDUCTION**

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In the previous works [1, 2] it was shown a noticeable electrocatalytic activity of conducting polymers (polyaniline, polypyrrole, etc.) toward the oxygen reduction reaction (ORR). ORR in such organic catalysts proceeds by two-electron mechanism and leads to the formation of  $H_2O_2$ . Our recent investigations have shown that some mixed oxides of transition metals (like  $MnCo_2O_4$ ,  $NiCo_2O_4$ ,  $FeCo_2O_4$ , etc.) are very active catalysts for ORR and  $H_2O_2$  decomposition. The main idea of this investigation was to create quite effective non-noble composite organic/inorganic catalysts working by four-electron mechanism of ORR in order to increase a catalytic activity and to escape a corrosion active  $H_2O_2$  from a battery (fuel cell). Also, it was found that such novel class of carbon as graphitized carbon black (GCB) is the most effective nano-structured carbon support for preparation of above-mentioned composite catalyst. Nano-sized inorganic part of catalysts was synthesized at the surface of GCB using sol-gel method. After that such inorganic part of catalysts was mixed thoroughly with an organic part of catalyst. Electrochemical investigations were performed using rotating disk electrode (RDE) at different speeds of rotation, which gives possibility to calculate a number of electrons "n" associated with ORR. Our investigations have shown that a composite organic/inorganic catalyst (polypyrrole/ $NiCo_2O_4$ /GCB) has demonstrated very high catalytic activity toward the ORR. The corresponding calculated number of electrons ( $n=3.8$ ) was almost the same, as for Pt catalyst ( $n=4$ ). Furthermore, such catalyst is not so sensitive for poisoning by different admixtures compared to Pt catalysts and could be used for oxygen reduction directly from an air in alkaline air-metal batteries and fuel cells.

Keywords: oxygen reduction, catalysts, batteries, fuel cells

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**EL-13****NOVEL MATERIALS FOR LITHIUM-ION BATTERIES**

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Lithium-ion batteries (LIBs) are the most promising devices for electrochemical energy storage. The more popular **negative active material** is usually flake graphite due to its excellent cycle life and low price. The main disadvantage of graphite is the relatively low specific capacity limited by the theoretical value  $Q_C^{\text{th}}=372 \text{ mA}\cdot\text{h/g}$ . Si, Sn, Al, and some other materials are the alternative materials for LIBs. However, they have not received a practical application, since their large theoretical capacity is accompanied by sharp drop of capacity during the first few cycles.

We have formulated the theoretical principles and developed some experimental composite anode materials [1, 2], which give the possibility to reach a high level of capacity during the stable cyclization. An optimal choice of novel **polymer binders** plays an important role for the development of such composites. Today  $\text{LiCoO}_2$  is the most popular **positive active material** for LIBs. However, it has a number of disadvantages (such as high cost; low specific capacity; toxicity and safety problems). Our team has an experience in synthesis and characterization of positive composite materials, based on the mixed oxides, as well as Fe phosphate. These materials can ensure quite high specific capacity, safety and acceptable price for LIBs. Recently, a new class of liquid electrolytes based on ionic liquids (ILs) has been discovered, which open new horizons for developing **novel composite electrolytes** for LIBs. They could ensure a considerable advantage over the traditional electrolytes due to their being non-flammable, having high electrochemical stability ( $> 5 \text{ V}$ ) and much lower toxicity.

Keywords: lithium-ion batteries, novel materials

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**EL-14**

**INFLUENCE OF THE HEAT TREATMENT OF STEEL Č.1531 ON THE  
CORROSION BEHAVIOR IN ACETIC ACID SOLUTIONS**

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The aim of this work was to investigate the corrosion behavior of heat treated medium carbon steel Č.1531 in acetic acid solutions. The corrosion behavior of heat treated and untreated substrates were characterized by current density-potential measurements. Polarization curves were performed in 0.5 and 5 mol-dm<sup>-3</sup> acetic acid solutions at room temperature. Open circuit behavior was also investigated. The heat treatment depends on the corrosion current, corrosion potential and corrosion rate of the steel and also to the values of the open circuit potential as a result of the different microstructure of the substrates. The obtained results were compared. The best corrosion resistance was obtained for the steel annealed at 300 °C.

The optical microscopy analyses were applied to examine the microstructure characteristics.

Keywords: corrosion, heat treatment, steel, acetic acid

## EL-15

### OPTIMIZATION OF PLATINUM/IRIDIUM RATIO IN THIN SPUTTERED FILMS FOR PEMFC CATHODES

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The work is devoted to preparation and investigation of the electrocatalytic activity of co-sputtered PtIr thin films towards the oxygen reduction reaction. The catalyst composition was controlled by varying the sputtering power of the Ir target in the range 20 – 100W at constant power of 100W for the Pt target. The films were analyzed applying SEM, XRD, EDX, XPS (physical characterization); stationary and quasi-stationary polarization curves, cyclic voltammetry and ac impedance (“*in situ*” tests performed in single PEMFC). The influence of the Pt/Ir ratio on the atomic interaction, morphology, and the resulting electrocatalytic activity was analyzed in detail. The contribution of the film content, morphology and the Pt/Ir electrocatalytic synergism to the electrode performance was evaluated. The optimal balance between the favourable effect of Ir addition and the lost of active surface sites due to substitution of Pt for Ir was established.

Key words: PEMFC cathodes, platinum, iridium, sputtered films.

## EL-16

### STUDY OF HOMOGENEOUS REDOX REACTIONS OF BIOCHEMICAL IMPORTANCE WITH VOLTAMMETRIC TECHNIQUES

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The aim is this work to develop a simple method for studying the charge transfer between redox centers of different species embedded in a single phase, which is one of the central chemical events in biochemistry. The studied reaction of this type is the oxidation of vitamin C with ferrocenedimethanol, analyzed by means of cyclic voltammetry at a glassy carbon electrode. It has been demonstrated that direct oxidation of vitamin C at the glassy carbon electrode undergoes at very high overpotentials, being attributed with sluggish electrode kinetics. In the presence of ferrocenedimethanol, the electrode mechanism undergoes according to  $E_rC'$  reaction scheme, where  $E_r$  refers to the reversible electrochemical oxidation of ferrocenedimethanol to ferroceniumdimethanol<sup>+</sup> cation, and  $C'$  designates the regenerative follow-up chemical reaction in which the latter cation is reduced back ferrocenedimethanol by means of homogeneous oxidation of vitamin C. Thus, the ferrocenedimethanol/ferroceniumdimethanol<sup>+</sup> redox couple serves as a redox mediator for catalytic oxidation of vitamin C, lowering down the energy required for electrochemical oxidation as well as increasing significantly the rate of electrode reaction. The reaction mechanism was analyzed by altering the sweep rate of the potential modulation and the concentration of vitamin C in the aqueous phase. The role of the aqueous medium was investigated by using Britton-Robinson buffers in a pH interval from 4 to 8. Due to acidic properties of vitamin C, the kinetics of the overall electrochemical mechanism is the most favorable in a slightly basic medium at pH 8.

Keywords: vitamin C, catalytic oxidation,  $E_rC$  electrode mechanism

## EL-17

### ELECTROLYTIC REFINING PLANT CONTROL SYSTEM

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#### Abstract

Monitoring and control of electrolytic refining processes demands timely transfer of process informations to the technologists. After the reconstruction of some facilities in the electrolytic refining laboratory in Mining and Metallurgy Institute Bor (Serbia), the demands for a new control system raised. Manual data collection using instrumentation on command tables and panels is replaced by microcontroller based real-time control system. Monitoring and control of electrolytic refining processes was performed with the use of Programmable Logic Controller (PLC). The simplest network consists of two nodes: one PLC and one workstation, typically a Personal Computer (PC), used for visualization and interaction with the process from a distant location. Process parameters are imported to PLC as standard current (4-20 mA) or voltage signals (0-24V DC). Monitoring PC has a serial connection (RS232) to PLC and acts as a server in network configuration. Information from PLC are then processed and the results are presented in real time or archived for later analyzes. All process parameters can be accessed from remote locations as well. The system is working on client-server principle.

Keywords: electrolytic refining, control system, temperature, real-time

**EL-18**

**ELECTRODEPOSITION OF SILVER POWDER FROM NITRATE  
ELECTROLITE**

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Electrical contact materials are used as contact members in a variety of switchgear applications, such as electrical switches, contactors, circuit breakers, relays, etc. Ultra fine metallic powders are commonly used in electrically conductive paste, solid oxide fuel cells and chemical catalysts, etc. In the manufacture of electronic devices such as hybrid integrated circuits and multiayer components], the technology of making conductive thick film from metal powders is of considerable importance.

The aim of this work was to investigate the process of electrodeposition of silver powder from nitrate electrolyte for usage in electronic. It was performed a series of experiments to test the solubility of silver powder in nitric acid and the effect of  $\text{Cu}^+$ ,  $\text{Pb}^{2+}$  and  $\text{Cr}^{2+}$  ions on the properties of the silver powder. At the concentration  $\text{Cu}^+=0.1 \text{ g/dm}^3$  the the average diameter of silver powder is 26.45-30.86  $\mu\text{m}$ . The morphology of silver powder obtained from nitrate electrolyte, was studied using the scanning electron microscope (SEM model: JOEL JSM-6610LV). Chemical composition of the silver powder was determined using the Energy Dispersive X-ray Spectroscopy (EDS). The EDS spectra for silver powder were recorded using the X-ray spectrometer, attached to the scanning electron microscope. Silver is detected using the EDS analysis. EDS spectra shows 100% of silver.

Keywords: silver powder, sedimentation curve, SEM, EDS

**EL-19****CURRENT DENSITY EFFECT ON THE SURFACE ROUGHNESS OF  
DECORATIVE GOLD COATINGS**

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The aim of this work was to investigate the effect of current density on thickness, surface roughness, visual appearance and morphology of electrochemically deposited gold decorative coating obtained from conventional cyanide electrolyte (AUROCIN DPB) and organic electrolyte, based on merkaptotriazole (Au-MT). Mechanically and chemically prepared brass samples are first nickered from acidic electrolyte. Nickel was a substrate deposit and, then the decorative gold coatings were deposited from two types of electrolytes at different current densities, at room temperature. Increase of current density has a positive effect on thickness of decorative gold coatings obtained from both electrolytes, for cyanide electrolyte (at  $D=0.1 \text{ A/dm}^2$   $b=0.08\pm 0.12\mu\text{m}$ , at  $D=0.4 \text{ A/dm}^2$   $b=0.04\pm 0.11\mu\text{m}$  and at  $D=1 \text{ A/dm}^2$   $b=0.08\pm 0.12 \mu\text{m}$ ) and for electrolyte based on merkaptotriazole (at  $D=0.1 \text{ A/dm}^2$   $b=0.03\pm 0.11\mu\text{m}$ , at  $D=0.5 \text{ A/dm}^2$   $b=0.04\pm 0.11\mu\text{m}$ ,  $D=0.83 \text{ A/dm}^2$   $b=0.05\pm 0.11 \mu\text{m}$ ,  $D=1 \text{ A/dm}^2$   $b=0.08\pm 0.12 \mu\text{m}$  and at  $D=1.7 \text{ A/dm}^2$   $b=0.04\pm 0.11\mu\text{m}$ ). In cyanide electrolyte, the surface roughness of gold coating is smallest for gold coating obtained at  $D=1 \text{ A/dm}^2$  ( $R_a=0.082 \mu\text{m}$  at  $0.1 \text{ A/dm}^2$ ,  $R_a=0.628 \mu\text{m}$  at  $0.4 \text{ A/dm}^2$  and  $R_a=0.052 \mu\text{m}$  at  $0.1 \text{ A/dm}^2$ ). Increasing the current density of Au-MT results in increasing of the surface roughness of gold coating ( $R_a=0.076 \mu\text{m}$  at  $0.1 \text{ A/dm}^2$ ,  $R_a=0.581 \mu\text{m}$  at  $0.5 \text{ A/dm}^2$ ,  $R_a=0.100 \mu\text{m}$  at  $0.83 \text{ A/dm}^2$ ,  $R_a=0.066 \mu\text{m}$  at  $1 \text{ A/dm}^2$  and  $R_a=0.053 \mu\text{m}$  at  $1.7 \text{ A/dm}^2$ ). The best coating roughness profiles are obtained at current density of  $1 \text{ A/dm}^2$  for both types of electrolyte. The coating thickness is measured using the apparatus type UPA XRF 200 A by X-rays reflection from gold atoms. Surface roughness is measured with a device TR 200 Surface Roughness Tester. Roughness parameters were computer readings. This was done using software :TR 200 Time Data View. Roughness is measured over a distance of 3.98 mm. The morphology of gold deposits, obtained from both electrolytes, was studied using the scanning electron microscope (SEM model: JOEL JSM-6610LV).

Key words: electroplating, decorative gold coating, current density, surface roughness, SEM

## EL-20

### **Pt-BASED BINARY ELECTROCATALYSTS FOR OXYGEN EVOLUTION REACTION IN WATER ELECTROLYSIS**

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Ebonex-supported Pt-based binary electrocatalysts (Pt-Fe, Pt-V) were prepared by wet sol-gel method using acetylacetonate precursors ( $M[(C_5H_7O_2)_n]_m$ ,  $M = Pt, Fe, V$ ) and deposited on nonstoichiometric titanium oxide support. The composition of the synthesized compounds was studied by X-ray diffraction (XRD) and X-ray-photoelectron spectroscopy (XPS) analysis. Their electrocatalytic activity toward oxygen evolution in water electrolysis was investigated using the common electrochemical techniques of cyclic voltammetry, steady state polarisation and long term performance tests.

The binary (Pt<sub>m</sub>M<sub>n</sub>,  $M=Fe, V$ ) catalysts supported on Ebonex exhibit higher mass activity than pure Pt, as Pt<sub>m</sub>Fe<sub>n</sub>/Ebonex demonstrates the highest one. The observed effects can be explained with the formation of solid solution between the metallic components (in case of Fe) and with realization of synergetic effect as a result of hypo-hyper-d-electronic interactions between catalysts and support, leading to changes in the electron density of Pt d-orbital.



**ENVIRONMENTAL CHEMISTRY (EN)**

## EN-1

### **FLY ASH AS COMPONENT IN COMPOSITES: POSSIBILITIES OF USING FLY ASH AS COMPONENT IN COMPOSITES REGARDING TOXIC ELEMENTS LEACHING PREVENTION**

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Fly ash, which is the residue from coal combustion in plants-operating-at-high-temperature, is severe hazard for the environment. The disposal of the fly ash exhibits a significant risk to the environment due to the possible leaching of hazardous pollutants, such as toxic metals. The only economic and sustainable solution for the pollution-prevention of the air, water and soil is to reuse the fly ash as one of the components in construction material composites. There is a risk of leaching even when fly ash is built-in the construction composites and the goal of this investigation was to prove that leaching concentrations of number of toxic elements is in range assigned by actual regulations. Fly ashes from various landfills, afterwards storage in closed silos, were applied in several composite samples (mortar, concrete and brick) without any physical or thermal pre-treatment. Testing composites were based on fly ash mixed with binder or with binder and aggregate. The leachability of the potentially toxic elements from the fly ash based products was investigated. The leaching behavior and potential environmental impact of the 11 potentially hazardous elements was tracked: Pb, Cd, Zn, Cu, Ni, Cr, Hg, As, Ba, Sb and Se. A detailed study of physico-chemical characteristics of the fly ash, with accent on trace elements and the chemical composition investigation is included. Investigation of mineralogical constituents of the fly ash is emphasized, due to the fly ash dependence of its origin. Thermal stability of crystalline phases was investigated with DTA. The microstructure of the fly ash and fly ash based composites was studied by means of SEM analysis. The overall results showed that most of the elements are more easily leachable from the fly ash in comparison with the fly ash based composites. The leaching of investigated toxic elements is within allowed range thus investigated fly ashes can be reused in construction materials production.

Key words: leaching, toxic elements fly ash, reapplication, construction composites.

## EN - 2

# THE POSSIBILITY OF USING NATURAL MATERIALS IN THE CONSTRUCTION

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Recently, a reference to ecology and sustainability becomes inevitable in all aspects of life. In this sense, a very important topic of energy and environmentally sustainable materials that are used for the construction of buildings, and one such material is straw. In Bosnia and Herzegovina yearly composes large quantity of waste during processing of agricultural plants. Large quantity of this waste is straw. A small part of straw is used for biofuel, the remaining part of straw is chopped and injected back in the soil. The purpose of this work is to explore the thermal properties of straw in order to produce an effective insulation material.

Thermal conductivity and thermal diffusivity of baled straw were determined. In order to measure the thermal conductivity of baled straw, hot plate method was selected, while for the measurement of thermal diffusivity the chosen method of exposure of the sample was step-changes in temperature. Hot plate method for dynamic determination of thermal properties of straw is moderate and evaluated using expanded polystyrene as reference material. Straw proved to be an excellent renewable insulation material which contributes to large savings in heating and cooling.

Keywords: natural materials, straw, thermal conductivity, thermal diffusivity.

**EN - 3**

**DISTRIBUTION OF LEAD IN WATER/SEDIMENT SYSTEM IN WASTE  
WATER OF METAL-WORKING INDUSTRY IN WEST SERBIA**

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The regions of the Republic of Serbia where the metal and metal-working industries are developed are sites where the presence of heavy metals is detected. The heavy metals are detected in the soil, water and especially in the sediment, which acts as an important source of metals in the aquatic environment and represents a “time bomb” threatening to pollute the entire ecosystem in the future.

In the town of Sevojno (western Serbia), there are two big active producers of copper and aluminum semi-products. The concentration of metals increases above the accepted levels over time and, through the food chain, it can also negatively affect people. The purpose of this work is to determine the concentration of the heavy metal – lead in the liquid and solid phase of the industrial wastewater, hazardous to the entire environment. The program package MAT LAB was used to define the distribution of lead between the liquid and solid phase depending on the distance from the point where the industrial wastewater is discharged.

Key words: heavy metals, lead, water, sediment, industrial wastewater

## EN-4

### RECYCLING AND ENVIRONMENTAL IMPACT

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Recycling process has high rank in the system of environmental protection and it must be given maximum attention to the trend of continuous improvement. In addition, the recycling process ensures reduced consumption of primary raw materials, recycling reduces the amount of waste disposed in landfills. Reused waste materials will be again placed into production, which is especially important in environmental protection. The aim of this paper is to highlight the importance of recycling processes on environmental quality, with a focus on the work of the recycling center in Podgorica, where the recycling process include recycling of paper, plastic, metal, glass and car.

By manner of returning to the process of re-use, recycling can be:

- Primary (recycling which after appropriate preparation of materials, the same is used for the production of new products or processing of used products to their re-use).
- Secondary recycling (recycling where conventionally unrecyclable processed materials using new technologies to the maximum possible efficiency).

Recycling is achieved by the following strategic objectives:

- Savings of raw material resources (all the materials come from nature and have them in limited quantities).
- Energy saving (not spending energy in the primary processes, as well as in transport and processes that monitor and get the extra energy combustion of materials that are recycled).
- Environmental protection (waste materials degrade living environment, and the recycling protects the environment).
- Creating new jobs (material recycling processes involve an investment of knowledge and labor, which creates the need for jobs).

Key words: recycling, waste, environment.

## EN-5

# SELECTION OF TECHNOLOGICAL DECISION FOR WASTEWATER TREATMENT IN THE ŽABLJAK MUNICIPALITY AND IMPACT ON THE ENVIRONMENT

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Existing situation in solving the collection, drainage and wastewater treatment in the municipality of Žabljak is not satisfactory, primarily because the wastewaters are discharged without their prior purification. With the construction of facilities for wastewater treatment in the municipality of Žabljak there will be improvements to the current situation. Due to the phased connection of population to the public sewerage system, the optimal construction of the WWTP is in two phases. In the first phase, it was planned to build the capacity of the WWTP approximately 2000 ES. In the second phase of the WWTP, potentially it may be necessary to extend the final capacity (3190-number of inhabitants of the Municipal of Žabljak is predicted by Physical – urban planning until 2021). The location of the planned construction of a wastewater treatment plant in the municipality of Žabljak is favorable, convenient to the terrain and in full compliance with the environment. The current system of separate sewerage in the inner area of the town of Žabljak (Phase I construction of the plant) is almost completely built. In the inner area of the town of Žabljak is collected and drained by wastewater from approximately 1200-1300 inhabitants, and the total number of beds at Planinka, Žabljak and other smaller hotels in the inner area of the town of Žabljak is approximately 700. Therefore, in first phase the WWTP with a capacity of approximately 2000 ES is needed. The location of the WWTP is next to depression, and there is no groundwater. Also, because of the proximity of depression there is a danger of high water.

It is planned the construction of a primary treatment (mechanical treatment in the emser-Imhoff tank) and secondary treatment (biological treatment - treatment based on active carbon). Tertiary treatment (nitrogen and phosphorus) is not provided, since the discharge of treated water into the abyss, and the assessment of eutrophication is not possible. Mechanical stage is designed as a classic emser, a biological level as percolator with extra ventilation. The plant will be built in two phases. In the first phase of the plant include the following facilities: 1) emser, 2) separator shaft, 3) typical Bioclere percolator (three prercolators) and 4) output shaft with measuring points.

Key words: wastewater treatment plant, primary treatment, secondary treatment.

## EN-6

# CATALYTIC OXIDATION OF 1,2-DICHLOROETHANE FROM GASEOUS FLUXES

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Organic compounds are frequent pollutants for the components of the environment (air, water, soil); those pollutants can come from both from natural and artificial sources. Once pollutants are introduced into the environment, they can have a major impact on the environment and increase the risks to human health.

Organic pollutants are very different in terms of chemical structure, molecular weight and hence in terms of physicochemical properties (solubility in water, resistance to degradation, etc.), and biological effects (toxicity or transformation metabolites toxic). The fate of persistent pollutants is dependent on some environmental factors (temperature, humidity, pH, presence of microorganisms), and specific physico-chemical properties of compounds (water solubility, vapor pressure, air-water partition coefficient).

Volatile halogenated organic compounds (VHOC) often occur as pollutants due to the emissions released from industrial activities. For instance, large emissions of 1,2-dichloroethane (DCA) are released from production process of vinyl chloride, trichloroethylene (TCE) and perchloroethylene (PCE). Also there are emissions during metallic surfaces degreasing, various halogenated hydrocarbons are released together to stripping air from oil degassing, and many very toxic compounds as phosgene, polychlorinated dibenzo-p-dioxines and polychlorinated dibenzofurans arise as by-products from incomplete combustion.

In this paper, some Pt/acidic support catalysts-like were prepared and tested during oxidation process of 1,2-dichloroethane. According to the obtained results, the advanced oxidation on Pt/acidic support catalyst-like can be considered an efficient procedure for the removal of volatile halogenated organic compounds in gaseous phase. The catalysts were obtained by impregnation method with solution excess. The prepared catalysts (Pt on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and HZSM5 support) were characterized in terms of catalytic activity by determining the mineralization grade of DCA (1,2-dichloroethane).

Keywords: volatile halogenated organic compounds, DCA, catalytic oxidation, Pt/acidic support.

## EN-7

# REMEDICATION OF BIODEGRADATION USING SYNTHESIZED NANO- AND MICROMATERIALS

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Paintings are probably the most beautiful way of expressing human creativity. Since ancient times, man has felt the need to express themselves through drawing. Mural paintings were part of human life since ancient times (it deserves mentioning in this context, the mural paintings from Lascaux cave, southern France, or the caves in Tassili Mountains, Sahara desert). Over time, painting support was diversified, so today the paintings appear on almost any type of support.

The paintings (both mural or on conventional support) are subject to degradation processes that require physical intervention techniques and/or chemicals to minimize destructive effects. The methods used must be able to prevent microbial contamination, or remove microorganisms already developed. The most common contaminant fungi (moulds) are *Aspergillus sp* and *Penicillium sp*, species that shows a greater tolerance to environmental factors. They are versatile species, which requires relatively little moisture, compared with bacteria.

The high degree of contamination is largely due to the fact that they produce spores easily dispersed by air currents. Mould is everywhere in nature, but it develops in humid, warm, dark and unaired conditions. The presence of fungi is closely related to the relative humidity of the environment in which the artifacts are kept in. If the relative humidity is too low, the chemical changes are minimized. However, the artifact will be predisposed to mechanical damage. If the relative humidity is high, the mechanical damage will be kept to a minimum, but this will encourage the growth of biological organisms. Those biological organisms are especially disastrous for paper artifacts.

To obtain remediation of the biodeterioration of the painting subjected to the study, we used a mixture of hydroxyapatite - nano-shaped barium hydroxide dispersed in isopropyl alcohol.

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Keywords: paper paintings, restoration, conservation, nanomaterials, biodegradation

## EN-8

# IMPACT OF A PLANT FOR THE PRODUCTION OF CONCRETE ON THE ENVIRONMENT

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Any work of nature or the environment, reasonable, socially beneficial and so on disturb the existing natural balance and have certain consequences and impacts on the environment. These effects may be temporary or permanent. In the case of temporary importance are the negative consequences that result from construction of the building facilities for the production of concrete.

Permanent consequences are reflected primarily in changing the landscape looks, usurpation of land, increased traffic flow, which increases the level of noise, air pollution etc.

In the production of concrete, due to machine working, emissions and dust during handling of the material necessary to produce concrete can be expected.

Sources of dust in the area of preparation of concrete and concrete products are:

- Delivering the cement unloading and storage in silos
- Transfer of aggregates
- Weighing and dosing
- The central mixer, emissions when loading trucks

Calculation of emission, diffusion and ambient level concentrations and PM particles with the production of concrete was conducted on the basis of specifications and standards to be met by the motors of working machines and the planned annual number of hours of machines, which are taken from the Investor.

All operating machines must comply with standards limit emissions of the EU Directive 97/68/EC which are defined standards for manufacturers. Implementation of regulations began in 1999 (EU Stage I), while the EU Stage II from 2001.

The application of more strict standards of permissible emission of EU Stage III and Stage IV began in 2006 and 2014 according to Directive 2004/26/EC. Total emissions are calculated below the limit values for non road machinery i.e. working equipment for the standardized allowable emissions of CO, HC, NO<sub>x</sub> and PM<sub>10</sub>. Thus, machinery to be used in the concrete factory, meets the specifications of standards EU Stage IIIB, according to which the calculation is done.

Given that the calculated emissions represent the maximum allowable, actual emissions will be less. Therefore, the calculated emission can be seen as so called "worst case" emissions.

Key words: plant for production of concrete, PM particles, diffusion, emission concentration, ambient level concentration.

## EN-9

# THERMODYNAMICS OF REACTIVE DYE ADSORPTION FROM AQUEOUS SOLUTION ON THE WASTE ASHES

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This paper describes the adsorption thermodynamics of textile reactive dyes from aqueous solution on the waste ashes formed by burning brown coal at the thermal plant.

Reactive dyes are identified as problematic agents in the waste waters because they are water-soluble. In the waste-water, they are found in larger quantities than the other kinds of dyes and mainly in the hydrolyzed form, so they cannot be so easily removed by the systems of the conventional treatments

The values of thermodynamic parameters are the actual indicators for practical application in the adsorption process. Based on characteristic diagrams are determined the thermodynamic parameters, enthalpy and entropy of adsorption, and based on those determined the Gibbs's free energy changes. In all cases, there is a negative sign of the thermodynamic parameters.

Entropy change (-2 to -3 J/K·mol) increases with increasing initial concentration of the adsorbate and decreases with increasing amount of adsorbent, suggesting that decreased disordered system at the interface of solid - solution during the adsorption of dye on the ashes. Negative values of free entropy changes indicate a reduction of unstable systems at the interface solidly - solution during the adsorption.

Free energy (-1.7 to -5 kJ/mol) decreases with the concentration of adsorbate discontinuous but continuously with increasing temperature, which is associated validity and spontaneous nature of the process. Negative values of free energy changes indicate the spontaneous nature of adsorption.

Small negative values of enthalpy change (-2 to -6 kJ/mol), provide for the physical nature and the energy stability of the reactive dyes adsorption by ashes and show that the adsorption process is taken to include the weak attractive forces that are exothermic.

Based on the thermodynamic data, it can be concluded that absolutely dominates the physical dye adsorption. Certain anomalies (several cases) in some indicators may indicate an error and the existence of, for example, chemical interactions in the system.

Key words: adsorption, thermodynamics, ash, reactive dye, entropy, enthalpy, free energy.

## EN-9/1

### KINETICS OF REACTIVE DYES ADSORPTION ON THE WASTE ASHES

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The aim of this paper is to present the adsorption kinetics of a typical reactive dye on the waste ash, which can lead to valuable data related to the possibility of wider application, for example with purification of the dyed waste waters. Sorption kinetics, which describes the rate of absorption of pollutants (dye), is one of the most important characteristic that defines the efficiency of sorption and the ability to use the adsorbent in controlling water pollution.

In order to investigate the mechanism of adsorption of reactive dyes from the textile industry on the waste ashes from city heating station by coal combustion, some characteristic constants of sorption are determined using Langergren's equation for the pseudo-first and pseudo-second order. United, kinetic models of pseudo-first order and pseudo-second order can provide a simple but satisfactory explanation of the adsorption process for a reactive dye.

Based on experimental results the following conclusions can be drawn:

- Kinetics of dye adsorption followed the model of pseudo-second order:  $q_{\text{exp}}$  experimental values are fully consistent with the calculated values  $q_{\text{cal}}$ , coefficient of determination in all cases of the model of pseudo-second order for dye is  $R^2 = 1$  (the model of pseudo-first-order  $R^2$  is below 1 or below 0.9).
- The rate constant of pseudo-second order decreases with an increasing initial concentration of dye and increases with an increasing amount of adsorbent - ash and temperature.
- Based on kinetic data, it can be concluded that physical adsorption dominates; for the applied dye since, according to the model of pseudo-second order, there were no restrictions due to possible chemisorptions, which would include valence forces through the sharing or exchange of electrons between adsorbent and adsorbate.

Keywords: adsorption, ashes, kinetics, Langergren's equation, reactive dye.

**EN-10****COPPER REMOVAL BY SORPTION ON FOOD-INDUSTRY RESIDUES**Mirjana Stojanović<sup>1</sup>, Zorica Lopičić<sup>1</sup>, Jelena Milojković<sup>1</sup>, Marija Petrović<sup>1</sup>, Časlav Lačnjevac<sup>2</sup>

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The high toxicity, persistence and bioaccumulation tendency of heavy metals have been recognized as serious environmental problem worldwide. Since the conventional methods for their removing are either too expensive for removing low concentrations of metals, or create large quantities of toxic sludge, the great attention has been given to the new technologies such as biosorption, technology that use cheap, abundant, organic waste for sequestering pollutants from contaminated mediums.

In this paper, the possibility of application of wasted biomass from food industry as potential biosorbent for copper removal was examined. The peach stone has been chosen for research focused on understanding the chemical and physical phenomena that are associated with the binding of copper to chemically untreated material. Only the hard stone parts were used, in different fraction sizes (ranging from whole stone to milled fraction of  $-1.0 + 0.5$  mm). Copper solution was prepared by dissolving  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (analytical grade) in distilled water using standard flasks.

Biosorption experiments were done using batch technique. The biosorption capacity of untreated peach material ranged between 1.2 to 2.3 mg of Cu/g adsorbent (depending on particle size-better results for smaller fraction). These results were obtained without pH adjustment, with starting Cu (II) concentration of 100 mg/l, using 1g of adsorbent in 100 ml adsorbate solution. These conditions didn't give high enough adsorption removal (up to 35%), so the next step was examination of adsorbent dosage for higher percent removal. With an increase of solid adsorbent amount, the removal of Cu (II) ions significantly increase, from the beginning 11.70 % (for M/V ratios 0.001g/ml) until the final 69.89 %, for the final ratio investigated (M/V= 0.3 g/ml). In opposite, the biosorption capacity drastically decreases, from the beginning 2.30 mg/g until final 0.13 mg/g for the M/V ratio of 0.5 g/ml. The third set of experiment involved variations of pH from 2 to 6, with M/V = 0.2 g/l, within 50 mg/l of Cu (II) solution. The results have showed that for these conditions, the highest pH value was obtained in the case of pH 6 (which was kept constant the entire time of sorption). The biosorption capacity for pH 6 was 4.32 mg/g with 86.45% of copper removal. All of this indicates that the conditions of biosorption should be thoroughly investigated and strongly controlled during the whole removal process.

Key words: water pollution, copper removal, biosorption, peach stone

## EN-11

**REMOVAL OF SOME BASIC AND ACID DYES FROM AQUEOUS SOLUTIONS BY ADSORPTION ONTO RICE HUSK ASH**Svetlana Genieva<sup>1</sup>, Mariana Tavljeva<sup>2</sup>, Velyana Georgieva<sup>2</sup>

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It is a fact, that many industries especially textile, leather, plastic, cosmetics, food, pulp, paper-making, dye and dyestuffs produce large volumes (fifteen percent of the total world production of dyes) of highly colored effluents from different steps in the dyeing and finishing processes. The release of these colored effluents in the ecosystem is a source of esthetic pollution. Molecular structure and coordination behavior of dyes impede their removal from effluents, because of the inherent stability of dyes towards light, heat and biodegradation, thus making the traditional treatment methods inappropriate.

The adsorption is the most popular physicochemical method for the removal of dissolved dyes from waste water. Active carbon, silica gel or  $Al_2O_3$  can be used as adsorbents but they are expensive and their recycling makes the treatment even more expensive. Rice husks are a major waste product from rice processing companies, and contain plenty of plant fibers, proteins and some functional groups such as carboxyl, hydroxyl, etc. that make the adsorption process possible. The controlled burning of the rice husks in air or in nitrogen atmosphere leads to the production of white and black rice husk ash, respectively, with different adsorption characteristics.

The adsorption of some basic and acid dyes from aqueous solutions was studied onto white and black rice husk ash. Batch experiments were carried out to determine the influence of some parameters such as initial pH ( $pH_0$ ), contact time ( $\tau$ ), adsorbent dose ( $m$ ) and initial concentration ( $C_0$ ) on the removal of dyes. The influence of the temperature increase on the adsorption was studied as well. Equilibrium isotherms were analyzed by Freundlich and Langmuir models using a non-linear regression technique. The values of the change of entropy ( $\Delta S^\circ$ ) and heat of adsorption ( $\Delta H^\circ$ ), and the change of Gibbs free energy ( $\Delta G^\circ$ ) were determined. The obtained data were analyzed and the optimal parameters for the adsorption were established.

Using the rice husk ash as an adsorbent can solve two ecological problems at the same time – utilization of rice husks and dye removal from waste waters. The obtained wastes from the adsorption could be burned in blast furnaces of the foundry industry.

*Keywords:* Basic and acid dyes; Rice husk ash; Adsorption isotherms; Adsorption thermodynamics

**Acknowledgement:** The work was financially supported by the project “Young scientists-2011” from National science fund, Ministry of education and science.

## EN-12

# THERMAL DEGRADATION OF RICE HUSK ON A FLUIDIZED BED REACTOR

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The present study is an attempt to establish the possibilities to obtain black rice husk ash (BRHA) and white rice husks ash (WRHA) via pyrolysis of wasted raw rice husks in a pilot plant fluidized-bed reactor at different conditions. The process course auto thermally, without outer fuel. The released heat may be used for steam obtaining or drying. The solid products obtained are characterized using TG/DTG/DTA analysis, X-ray diffraction patterns, SEM, FT-IR spectroscopy, and low temperature nitrogen adsorption.

Rice husks are an important by-product of rice milling process and are major waste product of the agricultural industry. Its major constituents are cellulose, hemicellulose, lignin, hydrated silica and ash. The organic part is composed approximately of 42.8%  $\alpha$ -cellulose, 22.5% lignin, 32.7% hemicellulose and other organic matter about 2%. The chemical analysis of the inorganic part in rice husks showed that the main component is amorphous silica. Rice husks has an average lower heating value of 13-16 MJ/kg and it is about one-third that of furnace oil, one-half that of good quality coal and comparable with sawdust, lignite and peat. Milling of 1 tone of paddy produces about 220 kg of rice husks, which are equivalent to approximately 150 kWh of potential power. This quantity of power is enough to produce electricity and steam for paddy drying. The energetic balance shows that utilization of rice husks as a renewable fuel may be convert paddy milling process from consumer to producer of energy.

The first purpose of this research was to produce rice husks ash from wasted rice husks through thermal degradation at different conditions using the fluidized bed technology. The controlled burning of raw rice husks in air on a fluidized-bed reactors leads to the production of WRHA containing almost pure ( $\geq 95\%$ ) silica in a hydrated amorphous form, similar to silica gel, with high porosity and reactivity. The controlled thermal degradation of rice husks in inert or poor of oxygen medium leads to the production of BRHA which contains different amounts of amorphous carbon incorporated with silica. This material has non polar surface very high porosity. The obtained WRHA and BRHA on a fluidized-bed bed reactor have good quality and may be used as adsorbent, filler of polymers, rubbers, cement and concrete or for other purposes.

Key words: Rice husks; Rice husks ash, Thermal degradation, Fluidized-bed reactor

## EN-13

### STUDY OF THE ADSORPTION OF SOME HEAVY METAL IONS FROM AQUEOUS SOLUTIONS ONTO RICE HUSK ASH

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Effluents from metallurgical and chemical industries, ceramics, electrogalvanization and textile industries are potential sources of water pollution by heavy metal ions. There is significant contamination of fresh water resources and an accelerating accumulation of toxic metal ions in the human food. The removal of the toxic metal ions from water is a very difficult task due high cost of treatment methods. Extensive research has been conducted for removal and recovery of heavy metals from wastewater and industrial water. Various methods exist for the removal of heavy metal ions from aqueous solutions: ion exchange, chemical precipitation, electrokinetic method. In recent year, sorption has been suggested as being cheaper and more effective than chemical or physical techniques.

An adsorbent can be considered as cheap or low-cost if it abundant in nature or is a by-product of waste material from waste industry. Agricultural residues, especially rice husk, the by-product of the rice milling industry are produced in large quantities as a waste, creating environmental problems. In this aspect in the present study as an adsorbent is used rice husk ash, prepared by controlled burning of the rice husks in air or in nitrogen atmosphere. This way can be solved two ecological problems simultaneously – utilization of rice husk and adsorption of heavy metal ions out of wastewater.

The goal of this study is to assess the adsorptive characteristics of heavy metal ions out of aqueous solutions onto white and black rice husk ash. The influence of some parameters such as initial pH, contact time, adsorbent dose and initial concentration on the removal of heavy metal ions were investigated. Adsorption process was found to be highly pH depend. Freundlich and Langmuir adsorption isotherms were applicable to the adsorption process, so using them the corresponding constants were calculated. The values of the change of entropy ( $\Delta S^\circ$ ) and heat of adsorption ( $\Delta H^\circ$ ), and the change of Gibbs free energy ( $\Delta G^\circ$ ) were determined.

Key words: Heavy metal ions; Rice husk ash; Adsorption isotherm; Adsorption thermodynamics

**Acknowledgement:** The work was financially supported by the project “Young scientists-2011” from National science fund, Ministry of education and science.

## EN-14

### WASTE MOULD SAND AS ADSORBENT FOR POLLUTED WATERS TREATMENT

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Water pollution by organic and inorganic chemicals is a major problem over decades. The presence of toxic compounds even at low concentrations can be an obstacle for the reuse of water so that removal of contaminants from groundwater or separation of contaminants present in polluted water has become a major focus of research and policy debate. There are a lot of techniques for the removal of various pollutants from waste waters (chemical oxidation, coagulation, aerobic or anaerobic biodegradation, solvent extraction, liquid membrane permeation, electrochemical precipitation, ion exchange, reverse osmosis, etc.). Among them, adsorption processes on activated carbon (AC) are currently proved to be an effective method for waste waters purification and have gained a lot of popularity. However, due to high costs of AC, the search of readily available and relatively inexpensive materials for pollutants removal is in progress.

Therefore, in this paper waste mould sand (WMS) from foundry industry was chosen to be tested as low cost adsorbent which can replace AC.

The adsorption of phenol, Cr(VI) and Ni(II) onto WMS has been studied using single component systems in aqueous solutions at 293 K. Batch studies were performed to evaluate the influence of contact time and initial concentration on the removal of heavy metal cations and phenol. Equilibrium isotherms for the adsorption on WMS were analyzed by Freundlich and Langmuir isotherm equations using linear correlation coefficients. Langmuir isotherm of adsorption for the systems studied gives a best fit with experimental observations. Capability of WMS to remove phenol, Cr(VI) and Ni(II) from aqueous solutions was demonstrated and thermodynamic analysis has shown that adsorption in systems under the study is spontaneous process.

It could be concluded that waste mould sand is potential low cost adsorbent that can be used in the purification of wastewater containing phenol or metal ions of chromium and nickel.

Key words: water treatment, waste mould sand, adsorption, removal of phenol, Cr(VI) and Ni(II)

**EN-15**

**RECYCLING OF NICKEL-BASED HAZARDOUS WASTE FROM THE  
PLANT OILS INDUSTRY**

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The results obtained during the recycling of spent nickel-based catalysts that are generated in the oil hydrogenation process are presented. Nickel-based catalysts are used for selective hydrogenation of the highly active plants oils. The used catalysts are classified in the H11 category of hazardous materials; they are deposited on the site and are potentially dangerous to the environment. Laboratory experimental research defined optimal conditions (temperature, time and solid-liquid ratio) and technological process of catalysts recycling. Hazardous waste is being converted to the category of non-hazardous, and extracted nickel as nickel-sulphate which represents commercial product. The degree of recovery of nickel is higher than 95%.

Key words: hazardous waste, used catalysts, nickel

## EN-16

# IMPACT OF HEAVY METALS FROM SHARRA LANDFILL, TIRANA, ALBANIA ON THE WATER SYSTEM

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Sharra landfill is designed and constructed in accordance with a quality system acceptable to Albanian legislation and operate on the basis of environment protection regulation. It functions in two stages - planning and operation.

Some specific standards regarding landfill's operation are applied regarding some important physico-chemical parameters in ground water and surface water control.

Some periodical controls are applied from the beginning of the landfill (before the year 2008) until now. It is clearly demonstrated that the parameters under investigation are decreased several times and actually fulfills the approved standards. Heavy metals are chosen as most important parameters that depict the toxicity. Very high level of heavy metals like  $Pb^{2+}$  (0.001 to 0.076 mg/L),  $Cu^{2+}$  (0.001 to 0.0283 mg/L),  $Co^{2+}$  (0.01 to 0.351 mg/L) are found at the beginning of the operation of the landfill. After intervention, the improvement on the leaching parameters of heavy metals content are evident, followed by the drastically decreasing of the heavy metal content in ground water and surface water systems.  $Pb^{2+}$  (<0.001 mg/L),  $Cu^{2+}$  (0.0007 to 0.0023 mg/L),  $Co^{2+}$  (n.d.),  $Cd^{2+}$  (<0.0001 mg/L) were drastically decreased by reaching the normal level of each element evaluated on the basis of Italian Standards, adapted as reference standard.

Key words: landfill, ground water, surface water, control, heavy metals.

## EN-17

# BIOLOGICAL TREATMENT OF WASTEWATER FROM GALVANIZING PROCESS

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Wastewater from technological process of galvanization contains oil and grease, organic compounds, secondary oils, anti-corrosion agents, metal ions, and others. Since they can have negative environmental effect, they must be treated before being discharged into the recipients. Primary wastewater treatment involves separation of free and non-emulsion oils and balance of waste water flow and oil concentration. In the second phase of waste water treatment, emulsified oil and large fractions of dissolved oil are being removed. After that, tertiary biological treatment based on fundamental biological processes that occur in nature is being applied. In order to obtain the strains of microorganisms, potentially useful for biological treatment, the isolation of microbial contaminants of waste water emulsions is being performed. The isolation of microorganisms has been performed on a selective medium that contained only mineral oil as a source of nutrients for microbial growth. In this procedure, it was assumed that isolates which grow on the surface with mineral oil have the possibility to degrade oil components, and therefore can be potentially applied for biological wastewater treatment. A special bacterial strain has been isolated from the emulsion waste water; this strain, on a selective media with mineral oil, produces white, glossy, opaque, convex colonies with an irregular border, the size 3-5 mm. Gram negative short rods with rounded ends, individual or in pairs, have been observed on a microscopic preparation. According to the biochemical characteristics of the isolates and comparison with the characteristics of Gram negative bacteria, it was assumed that the isolated bacteria belong to the genus *Pseudomonas*.

Key words: galvanization, treatment, waste water.

## EN-18

# ALTERNATIVE FUELS IN CEMENT INDUSTRY – RENEWABLE AND SUSTAINABLE SOURCE OF ENERGY

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Faced with limited availability of conventional fuels and raw materials and even more uncertain future in the same regards, the modern society is searching for sustainable solutions how to use and preserve natural resources and at the same time to minimize the impact to general environment. Especially valuable are practices by which waste products from one industry or activity become the raw material or energy source for another.

Following TITAN Group environmental policy, Cementarnica Usje initiated Investigation Study on availability of wastes and their classification as a potential alternative fuel source. The findings in that study and experiences of cement industry in developed regions where usage of different waste streams as alternative fuels is safe and favourable solution will be presented.

Selected waste streams and by-products with recoverable calorific value can be used as fuels in a cement kiln replacing a portion of conventional fossil fuels if they meet strict specifications. Depending of its availability in the region and applied production technology, different pre-treated products can be used as alternative fuels (AFs). In general, the most common used AFs are: biomass (rice husk, wood chips, nut shells etc.), Refuse Derived Fuels (RDF) from Municipal Solid Waste, waste oils, spent solvents, bone meal, sewage sludge etc.

Characteristics of cement kilns and working condition for production of clinker make the cement industry ideal installations (better than incinerator) in which AFs can be valorized and co-processed with no impact to the environment.

Concrete made from cement manufactured using alternative fuels has the same properties as concrete made from cement manufactured using fossil fuels. The heavy metals in the cement are bound in the clinker components, and they are chemically bound in the alkaline reaction products formed when cement reacts with water to give the concrete its strength. This fixation as well as the high density and low permeability of concrete result in very low potential for release of heavy metals.

Using alternative fuels in cement plants is an important element of a sound waste management that creates benefits to the environment, society and industry. That is a proven and well-established practice in most of the European cement industry for more than 15 years.

Keywords: Cement kilns, Alternative Fuels, Solid Waste Management, biomass, Refuse Derived Fuels.

## EN-19

### **STUDY OF ATMOSPHERIC DEPOSITION OF HEAVY METALS IN ELBASAN AREA, ALBANIA, BY ACTIVE MOSS BIOMONITORING TECHNIQUE**

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This study is focused on the evaluation of the air pollution level of Tirana, through the active moss biomonitoring technique, by using *Hypnum cupressiforme* in Elbasan urban area, Albania. Moss bags were exposed without irrigation for 6 months at 14 sites of Elbasan area. Heavy metals (Cu, Pb, Zn, Mn, Fe and Cd) were determined by atomic absorption spectrometry by using flame/and or electrothermal system. CVAAS was used for mercury determination and atomic emission spectrometry for K and Na determination. The target elements in this study are Cd, Hg, Cu, Pb, Zn and Mn. For better interpretation of data, the elements Fe, K and Na were also included. The area is being moderately polluted due to the high vehicular emissions, iron metallurgy, chromium smelter plant and cement industry. The comparison with unexposed moss allowed us assessing the enrichments factors in exposed moss samples for all determined elements. Most of heavy metals show high accumulation near cement factory and metallurgic complex sites. Therefore, we have been tried to categorize different places in the city on the basis of mentioned metal concentrations in the mosses and data statistical treatment. To distinguish different factors affecting the mobility of elements correlation and multivariable analysis was carried out.

Key words: Moss biomonitoring, heavy metals, air pollution.

**EN-20**

**LEACHATE OXYGEN PARAMETERS  
AS KEY- FACTORS IN THE MSWL MATURING DETERMINATION**

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Within a municipal solid waste landfill (MSWL) a complex processes of physical, chemical and biological character exist, leading to the formation of unwanted refuse being degraded and/or transformed. Rain waters percolate through the disposed solid wastes on the landfill, creating leachate carrying contaminants to the environment. An extended investigation on the leachate content during the period of one calendar year (spring, summer, autumn and winter) was made. Beside the pH and the content of heavy metals in the leachate, the variation of the oxidation parameters ( $O_{2(diss)}$ ,  $BOD_5$ , COD) were carefully checked and subsequently the relative  $BOD_5/COD$  ratio in the landfill leachate determined. According to the experimentally gained results and comparison with the pertinent literature data it was possible to determine the different phases of maturing of the studied municipal solid waste landfill. The analyses point out that the variation in the oxygen parameters values are crucial in determination of the different phases in MSWL maturing.

Key words: municipal solid waste landfill, oxygen parameters, leachate content, landfill maturing

## EN-21

### **DETECTION OF SOME HEAVY METALS IN WATER PRESENT IN THE WATER SUPPLY SYSTEM STUDENCHICA IN KICHEVO ON THE BASIS OF DOMESTIC WATER HEATER SCALE**

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The quality of the raw water spring of Studenchica and drinking water in Kichevo has been investigated by means of radiological, microbiological and parasitological analysis. Also, the analysis of presence of pesticides in raw water from the spring of the Studenchica river was performed. Continuously, certain physical, chemical and microbiological parameters in drinking water at seven measuring points through the previously established measuring network were controlled. In order to obtain a real picture on the quality of the drinking water passing through the water supply system in Kichevo, an additional analysis of the chemical composition of the solid scale formed in domestic water heater was performed. The application of the AAS and AES-ICPS pointed out that the water contains significant quantities of heavy metals mostly zinc as well as iron and lead in smaller quantities. The X-ray analysis applied on solid scale showed that Zn appeared in the form of smithsonite ( $ZnCO_3$ ), zincite ( $ZnO$ ) and elemental Zn. Since the zinc concentration in the raw (untreated) water was far lower than maximal allowed value, the appearance of zinc in the solid scale from domestic water heater can only be a product of leaching of zinc from the galvanizing metal layer in the transporting pipes of the drinking water supply system.

Key words: drinking water, heavy metals, water supply system, solid scale, AAS, AES-ICPS, X-ray

## EN-22

### DETERMINATION OF HEAVY METALS CONTENT IN AGRICULTURAL SOILS IN URBAN AREA

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Heavy metals are group of elements geo-chemically described as trace-elements with density higher than  $6 \text{ g/cm}^3$ . The most important elements and their compounds, known as the potential environmental danger when present in soils in higher concentration are As, Cd, Cr, Cu, Hg, Ni, Pb and Zn. These elements are very dangerous for human health as well. Within this study the investigation of the presence of heavy metals freely released in the surrounding from the Cement Factory “Titan”, Skopje and the chemical industry “OHIS”, Skopje, thus polluting the local agricultural soil fields was performed. XRD and ESA methods were subsequently applied in order to determine the quality and character of the soil, and the presence of heavy metals in the investigated region. Obtained data are presented as XRD diffractogram showing the soil character. ESA analysis outlined the several times higher concentration in Pb, Cr and Ba than prescribed by the rules for allowed concentration of heavy metals in soils of urban area.

Key words: heavy metals, agricultural soils, pollution, non-proper disposal, protection

## EN-23

### PHYSICO-CHEMICAL BIODIVERSITY AND BIOLOGICAL MONITORING OF THE VIT RIVER, BULGARIA

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The Vit River is related to the Danube water collecting region. The valley of the river from the sources to the State border is indicated as a region with middle and high degree of importance in respect of the data about the species richness, the endemic and rare taxons. The Vit River is one of the biggest tributaries to the Danube River, which springs from the Balkan Mountain, Northern Bulgaria.

The physico-chemical and hydrobiological monitoring of the river was performed using chemical analysis of basic physico-chemical indicators and freshwater organisms as bioindicators. The results of the first for Bulgaria ecomonitoring researches, carried out during three seasons (spring, summer and autumn) of 2011 in 3 biotopes (Biotope 1 – before village of Yasen; Biotope 2 – after village of Opanec; Biotope 3 – Tuchenitsa, after town of Pleven; Biotope 4 – after town of Gulyanci) of the Vit River valley in the direction middle – lower course trough tests performed to find chemical pollution, are presented; analysis of the biological diversity of bioindicative groups of organisms (macrophytes, bioindicative macroinvertebrate fauna), occupying different trophical levels in the researched freshwater ecosystems.

The physico-chemical monitoring was made on the basis of indicators of: acidity, insoluble substances, electrical conductivity, biological oxygen demand (BOD<sub>5</sub>), chemical oxygen demand (COD), nitrate ions, sulphate ions, copper, lead, nickel, etc. The results may be applied in the various monitoring systems for assessment and forecast of the Vit River condition and of the Danube water collecting region.

Keywords: Monitoring, Heavy Metals, Bioindication, Macrozoobenthos, Vit River

## EN-24

### **BIODIVERSITY AND HEAVY METAL POLLUTIONS IN FRESHWATER ECOSYSTEMS IN BORDER AREAS FROM TUNDZHA RIVER, BULGARIA**

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The purpose of this study has been to investigate the biological variety of the freshwater ecosystems from the Tunzha River and to make an ecological evaluation of their condition. The Tunzha River is related to the Aegean water collecting region. The analyses have been made in the region from the border areas on the river Tunzha (biotopes Elhovo, Konevec). For an ecological evaluation of the situation of the analyzed freshwater ecosystems, principal biotic indexes have been fixed.

Ecological research has been performed on the helminths communities of chub (*Leuciscus cephalus* L., 1887) in the Tundzha River. The tendencies in the seasonal variation of the helminths communities of *L. cephalus* in the Tundzha River are presented through relevant biotic indices and statistic comparisons, based on standard non-parametric tests. Basic abiotic (acidity, insoluble substances, electrical conductivity, nitrate ions, sulphate ions, lead, etc.) and biotic characteristics (total number of specimens, prevalence, mean intensity, etc.) of the water habitat in the area under research. The bioindicative hydrobionomic macroinvertebrate fauna is characterized. An assessment of the status of the biocenoses subject to this research has been carried out.

The studies from could be used in various monitoring systems for reported on pollution's on the water environment and the organisms, inhabited the anthropogenous ecosystems.

Keywords: Bioindication, Heavy Metals, Chub Parasites, Tundzha River, South Bulgaria

## EN-25

# GOLD CATALYSTS ON CO-MODIFIED CERIA FOR COMPLETE BENZENE OXIDATION: RELATIONSHIP BETWEEN REDUCIBILITY AND CATALYTIC ACTIVITY

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The dangerous for the human health volatile organic compounds (VOCx) are considered as great contributors to the air pollution. The toxic benzene is extensively applied in the industry. Its complete oxidation is often studied as a model reaction of VOCs combustion since benzene is a very stable organic molecule. Nanosized gold catalysts on different reducible supports have been reported as promising systems for total oxidation of VOCs.

Mixed  $\text{CeO}_2\text{-Co}_3\text{O}_4$  supports (5, 10 and 15 wt%  $\text{Co}_3\text{O}_4$ ) were prepared by mechanical mixing of calculated amounts of cerium hydroxide and  $\text{Co}_3\text{O}_4$ . Gold (3 wt%) was loaded by deposition precipitation method. Very high catalytic activity in the reaction of complete benzene oxidation (CBO) was observed over gold catalyst supported on ceria doped with 10 wt%  $\text{Co}_3\text{O}_4$ . It was higher than that of gold/ceria catalyst and significantly higher compared with that over gold catalysts on ceria doped with 5 or 15 wt%  $\text{Co}_3\text{O}_4$ . For all mixed supports the presence of separate  $\text{Co}_3\text{O}_4$  phase and some contraction of ceria lattice showing Co-modification of ceria were observed by XRD data. The obtained Raman spectroscopy results were not relevant for making supposition about the effect of Co-dopant amount on the defects in ceria structure. The HRTEM/HAADF results revealed that the ceria modification with 10 wt%  $\text{Co}_3\text{O}_4$  was favorable for gold loading with higher dispersion. The differences in the reduction behaviour were commented not only by the obtained TPR profiles but also on the basis of hydrogen consumption of the individual reduction processes of ceria and the separate Co-phase. The highest reducibility, e.g. ability of oxygen supplying of gold catalyst on ceria doped with 10 wt%  $\text{Co}_3\text{O}_4$  was in agreement with the results of higher gold dispersion and correlates with the highest oxidation activity in CBO over this catalyst.

Keywords: gold catalysts, ceria doped with  $\text{Co}_2\text{O}_3$ , complete benzene oxidation, reduction behavior

## EN-26

### DETERMINATION OF ORGANIC POLLUTANTS FROM RIVER WATER USING PASSIVE SAMPLING SYSTEM FOLLOWING GC/MS

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The contaminants present in water environment may include complex mixtures of chemical compounds. The fate of contaminants is largely unknown, however, the limited data available suggests that many of these chemicals survive treatment and some are returned to their biologically active form via of metabolites. Traditional monitoring programs consist of collecting samples of environmental water at specific points of time, performing sample enrichment followed by instrumental analysis (GC, GC/MS or HPLC-MS). The traditional Solid Phase Extraction (SPE) sampling methodologies have many inconvenient features. The volume of water sampled may be insufficient to satisfy the detection limit requirement. Normally water samples represent only those contaminants present at the time of sampling. Transient occurrence of selected contaminants in wastewater may result in temporal changes in the chemical quality of effluent discharged to neighboring streams. Without sufficient repetitive sampling, it may be impossible to formulate estimates on the time-weighted average concentrations of the contaminants of interest. Passive samplers offer an attractive alternative to traditional sampling methods. Two of the most commonly used passive samplers for organic contaminants are the semi-permeable membrane device (SPMD) and the polar organic chemical integrative sampler (POCIS). Passive sampling can be defined as a sampling technique based on free flow of analyte molecules from the sampled medium to a receiving phase in a sampling device. The net flow of analyte molecules from one medium to the other continues until equilibrium is established in the system, or until the sampling period is stopped. Estimation of pollutant concentrations in water can be done according to dedicated equations having in account the mass of the sorbent in the POCIS, specific sampling kinetic constant and is the sampling period. The present papers concern is to make a comparative study between the results obtained by analyzing the pollutants from same places of river water (Prut River) using POCIS passive sampling system and grab sample mode.

Key words: Passive Sampling, POCIS, GC/MS, River Water

**EN-27****OILY WATER TREATMENT USING A STEADY-STATE FIBER-BED  
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Oily waters may contain heavy hydrocarbons such as tars, grease, crude oils, diesel oil, lubricants, cutting liquids, and light hydrocarbons, as well as fats, vegetable oils or fatty acids. Selection of separation technique depends on several factors, the most important being oil solubility in water. Namely, part of the oil is always soluble while the other part is dispersed in water. In case of dispersed oil, it is important to know its pour point. When the working temperature is higher than oil pour point, the dispersion contains two immiscible liquids. In such case we deal with a liquid–liquid system.

Steady-state bed coalescers are comfortable solution for the separation of unstable emulsions. The use of fiber-bed coalescers, due to their high efficiency and simple construction, is getting increasingly attractive in the industry. Bed coalescers consist of two sections: bed and settling section. Separated oil, with low concentration of water, collects on the top of the settling section and is discharged discontinuously. However, their design is still based on experimental data.

We investigated separation efficiency of oil from model oily water with constant inlet concentration of 500 mg/l using waste polymers as a filter media in bed coalescer. The model emulsion was prepared by continuous stirring with a stainless steel impeller in two tanks. The emulsion was continuously forced through the bed by a membrane dosage pump for chosen fluid velocities range from 19 to 60 m/h. A selected velocity was kept constant for 1 h, and composite samples were taken in the last 15 min in 5 min intervals. The working temperature was 20 °C and it was constant, too. The main characteristics of oils: density, mean molecular weight, viscosity, neutralization number and pour point were measured for all four investigated oil phase. The separation efficiency was calculated on the basis of the oil concentration in the influent and effluent. Effect of bed bulk density, fluid velocity and nature of dispersed oil on coalescence efficiency was investigated. Only over bed bulk densities of 50 kg/m<sup>3</sup> and 180 kg/m<sup>3</sup> the separation efficiency was independent of the fluid velocity and it was in the range from 99.56 % to 98.47 %. Separation efficiency over three other bed bulk densities was lower then 90 %.

Key words: bed coalescer, oily water separation, fiber bed

## EN-28

### DOES WILDFIRE AFFECT HEAVY METALS CONTENT IN HERBS USED IN TRADITIONAL MEDICINE?

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The mountain Vidlic (Serbia 43°10'16.7"N; 22°39'06.0"E) has been very popular area for collection of herbs, traditionally used for treatment of many diseases. A ten-day large-scale wildfire that occurred in the summer 2007 on the Vidlic Mountain and affected more than 2500 hectares of forests, meadows and rocky meadows, placed into the focus the possible impacts on quality of the environment.

Considering the wide usage of wild herbs for human consumption, potential elevated levels of heavy metals may pose a health hazard and in that way their application can be limited or even forbidden. The study of Cu, Zn, Pb and Cd content in selected herbs (*Calaminta nepeta*, *Satureja montana*, *Salvia austriaca* and *Achilea millefolium*.) was conducted, in species harvested in the post fire area, after one year of fire occurrence. Control samples were collected in the areas that were not affected by the fire.

The plant samples were washed in distilled water, dried at 105 °C for 24 h and grounded to obtain a homogenized powder. The samples were then digested with HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>. The concentrations were measured using ICP-OES.

The average content of Zn, regardless of habitat, is in the range of 20-80 ppm, corresponding to the normal content of Zn in plant material. Copper has been presented in higher concentrations in plant samples from non affected areas (except for *C. nepeta*). In almost all analyzed plants, Pb content is below the limit. The highest content of Cd was found in herb *A. millefolium* from post fire area. Content of Fe in the analyzed plants was in the range 21-241 ppm. The highest content of Fe (241 ppm) was determined in plant species *S. austriaca* from the area that was affected by fire, while the lowest content was in the plant species *A. millefolium* (22 ppm).

Wildfire in most cases, have been the cause of increased content of studied heavy metals, but all of the obtained values were bellow the prescribed limits. This fact can be contributed to the absence of harmful heavy metals doses in the environment, before wildfire, rather than to air and hydro transport of them.

Key words: heavy metals content, ICP-OES determination, wildfire impact

## EN-29

# USING ICP INSTRUMENTATION FOR FAST AND ACCURATE DETERMINATION OF Cr, Mn, Zn, Cu, Pb AND Cd IN SOME VEGETABLES

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Heavy metals, coming from various sources and accumulated in edible plants can have harmful effects on health if consumed. The scope of this study was to investigate the effects of potential pollution sources on heavy metals content in spicy vegetables: parsley (*Petroselinum crispum*) and celery (*Apium graveolens*) collected from district of Serbia: Bor (surrounding areas of copper mine), Pirot (nearby international highway), Rasina (nearby river and in urban area), K. Mitrovica (surrounding areas of lead mine) and Toplica (assumed unpolluted areas).

Metal contents were determined using ICP-OES. The quantification was performed using an external calibration with multielemental Merck standard solution

The content of Cd, Pb and Cr in the parsley samples is the largest in Pirot district, in the locality Dolac was  $0.22 \pm 0.01$  ppm and  $16.70 \pm 0.08$  ppm and  $53.01 \pm 0.17$  ppm respectively. The locality Slatina in the Bor district is characterized by the highest content of Cu and Mn in the parsley samples  $25.59 \pm 0.38$  ppm and  $30.45 \pm 0.20$  ppm. Zn content in parsley is the largest in the samples from Rasina district  $41.76 \pm 0.00$  ppm.

High concentrations of Cr and Cu are in the celery samples from K. Mitrovica district,  $15.94 \pm 6.33$  ppm and  $22.31 \pm 7.04$  ppm respectively. The locality Vrbnica in the Rasina district is characterized by the highest content of Cd and Mn in the celery samples  $1.98 \pm 0.01$  ppm and  $28.05 \pm 1.70$  ppm. The content of Pb and Zn in the celery samples is highest in Bor district,  $3.68 \pm 0.00$  ppm and  $48.12 \pm 0.00$  ppm.

The examined vegetables showed various affinity for heavy metal intake in the same environmental conditions, which can be linked to their different physiology. Elevated levels of toxic heavy metals were found in samples from areas nearby motorways in comparison to areas exposed to heavy metals pollution longer time such as mine's surrounding areas.

Keywords: ICP-OES determination, heavy metals content

## EN-30

# PROCESS OF PURIFICATION OF MOTOR OIL AND ITS USE AS AN ECOLOGICAL FUEL

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Used motor oil can be cleaned by a suitable chemical treatment in order to obtain purified motor oil that can be re-used as motor oil for vehicles or ecological fuel. The need for recycling of the used motor oils initiated the idea for its cleaning with a simple, rapid, environmentally safe, secure and inexpensive process. Technical and technological procedure which does not require much time, human resources and large workspaces is used. The products which are used for motor oil purification are products that are readily available on the market. The process begins by filtration which removes mechanical impurities. The process of filtration is followed by the process of the chemical treatment using concentrated acid and alkali. As result, the residual amount of adsorbed water and ions were removed. The process ends with repeated filtration using the same filter as in the initial step.

The resulting oil is purified to satisfactory quality and can be used as an ecological fuel. Purified oil can be used as fuel in central heating systems and provides reduced heating costs and a cleaner environment in terms of reducing exhaust fumes.

Key words: motor oil, purification, ecological fuel

## EN-31

### **EVALUATION OF BIODIESEL ENVIRONMENTAL IMPACT BY GREEN QUALITY FUNCTION DEPLOYMENT AND ECO-INDICATORS**

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Worldwide global requirements for clean and save environment have put significant challenges to the companies that want to meet the strategies for sustainable development, as well as the customer and the market needs. The list of critical issues that the manufacturing firms should consider to remain competitive are production of high quality products, lowering costs and prices, decreasing product cycle time and protecting the environment.

Depletion of fossil fuel sources has forced many countries to include biodiesel production in their energy strategies. Until now, the environment assessment of biodiesel was focused on energy demand and greenhouse gas emissions, while small attention was given to other impacts.

The main objective of this research is to develop a decision-oriented biodiesel life cycle that enables the integration of cost and quality factors together with eco-indicators at the first stages of product development. Two alternatives will be consistently compared and the optimal concept will be recommended.

Keywords: environmental impact, biodiesel, GQFD, eco-indicator

## EN-32

### FROM PLASTIC WASTE TO ENERGY

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During the last decades, the increased focus on energy resources and climate has changed the perception of waste, especially of plastic waste. The main goal of the new so-called clean technologies is waste prevention. Today, it is generally accepted that waste can be beneficial to the environment provided that the waste is managed properly. The waste management is not an isolated process but interact with the environment. Especially interactions with the energy sector have a profound effect. Optimal utilization of plastic waste and energy recovery is a highly prioritized treatment option in Europe. Energy from waste accounts for approximately 20% of the annual heat production and 4% of the electricity production.

In this work, the energy potential of the plastic waste will be defined depending on the type of waste content as well as on the type of plastic waste. The environmental impact assessment (EIA) will be done using life cycle assessment (LCA), material flow accounting (MFA) and eco-indicators (Eco-it). EIA of plastic waste to energy process will be compared with the EIA of the material recycling.

Keywords: plastic waste, energy recovery, environmental impact assessment, eco-indicator

## EN-33

# DEVELOPMENT OF COMBINED TANNING TECHNOLOGIES WITH INCREASED WASTE WATER BIODEGRADATION

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In recent years ecological aspects have been crucial for improving and developing new technologies for leather manufacturing. The process of tanning is one of the most important in leather manufacturing, which determines the properties of leather. This process involves a considerable number of chemical substances harmful to both people's health and environment. In this respect chromium compounds are especially hazardous. The alternative technologies can include tannages based on vegetable polyphenols that are vegetable tannides, or synthetic organic tannages. To evaluate the influence of existing and promising tanning technologies is possible with the help of determining such factors as biological oxygen demand and chemical oxygen demand of (BOD and COD, correspondingly). To evaluate the capability of the substances for biodegradation is possible by determining the BOD : COD ratio.

An phosphonium-tannide technology has been developed for sheepskin tanning hides, which involves the usage of mimosa tannides, preliminary processing with phosphonium compounds, instead of chromium compounds traditionally used for this purpose. Besides, using the aluminium compounds promotes increasing the thermal stability of the derma. The liquid of the phosphonium compounds and the tanning vegetable-aluminium solution are capable of biodegradation on the level of some proteins, which is evidenced by the ratio BOD: COD = 0,49 and 0,58 mgO<sub>2</sub>/l, correspondingly. Besides, the absence of chromium compounds in the liquid waste improves the biodegradation of the other substances. An aldehyde-aluminium-chromium technology has also been developed for tanning cattle hides, which provides decreasing consumption of chromium compounds by a factor of 2 compared with existing technologies by partial replacement of chromium compounds with aluminium compounds and glutaric aldehyde. Implementation of the technology provides a rather low content of chromium compounds in the exhaust solution, which makes the waste water purification much easier and improves the environment.

Key words: environment, biodegradation, tanning technologies.

## EN-34

### SPATIAL DISTRIBUTION OF HEAVY METALS AND SOME LITHOGENIC ELEMENTS IN SOIL FROM COPPER CONTAMINATED AREA

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Monitoring with soil samples was conducted in area with intensively exploitation of copper minerals (copper mine “Bučim” near Radoviš, Republic of Macedonia). Soil samples from the surface layer (top soil) and from the deep layer (bottom soil) at the same locations were collected. Characterization of 18 elements contents was done: Al, As, Ba, Ca, Cr, Cu, Ga, Li, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V and Zn. Close mine environment was concern with higher Cu contents (max. value obtained of 1200 mg kg<sup>-1</sup>), but the rest of the area was characterize with median value for copper content of 23 mg kg<sup>-1</sup>. The enrichment factor of TS/BS for Cu was 2.8 for whole study area and ~10 times for very close mine environment. For the rest of the potentially anthropogenic elements (Cr, Ni, Pb, V, Zn) no significant enrichment factors were found for TS/BS relation. The lithogenic elements (Al, As, Ga, Fe, Li, Mg, Mn, Na, Sr) content showed stability in the vertical direction (TS/BS); but in a across direction, variability of element contents undergoes with the geology of the region. Characterization of element contents is in order of the type of land use. Maximum values for Cr, Ni and Pb were found in cultivable area (290 mg kg<sup>-1</sup>, 190 mg kg<sup>-1</sup> and 130 mg kg<sup>-1</sup>, respectively). Coefficients of correlation for the contents of the elements are represented in the matrix of correlation coefficients. With the factor analysis the distribution was reduced to three synthetic variables, which showed linkage in terms of geochemical similarities: F1 (Mg-Cr-Al-Fe-Ca-Mn-Ni), F2 (Pb-Ni-Li-Mn), F3 (Ba-Sr-K) and F4 (Zn-Ga-As-Fe) including 75% of the variability of analyzed elements. Spatial distribution of As, Cu, Pb, V and Zn showed that higher contents of these elements are deposited in mine vicinity; due to dust distribution from ore and flotation tailings. Distant areas were not concerned.

Keywords: Heavy metals, spatial distribution, copper mine, soil pollution, Republic of Macedonia

## EN-35

# MOSS BIOMONITORING OF AIR POLLUTION WITH CHROMIUM IN CROATIA

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Biomonitoring of air pollution by using moss samples is widespread in Europe. More investigations and surveys were carried out in order to examine air quality. Croatia participated twice in a moss survey in the framework of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops with Heavy Metals in Europe (UNECE ICP Vegetation). For the first time Croatia participated in 2006 and the second time in 2010. During the summer and autumn of 2010, moss samples were collected from 96 sites evenly distributed over the country.

Chromium was determined by using atomic emission spectrometry with inductively coupled plasma (ICP-AES) after previous microwave digestion of moss samples. The median value of chromium content ( $1.83 \text{ mg kg}^{-1}$ ) was found to be lower than the same value in 2006 ( $2.8 \text{ mg kg}^{-1}$ ). Chromium content ranges from  $0.41 \text{ mg kg}^{-1}$  to  $7.78 \text{ mg kg}^{-1}$ . Maps of distribution of chromium from the surveys in 2006 and 2010 will be compared. Some anthropogenic sources in/around Zagreb, Sisak and Kutina were found.

Key words: air pollution, moss biomonitoring, chromium, ICP-AES, Croatia

**N-36**

**DISTRIBUTION AND MOBILITY OF HEAVY METALS IN *Thymus alsarensis* Ronniger IN THE REGION OF As-Sb-Tl MINE ALLCHAR, REPUBLIC OF MACEDONIA**

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Alchar mine is an abandoned antimony-arsenic-thallium deposit located on the north-western part of Kožuf Mt., Republic of Macedonia. The locality of Allchar (Alšar) is unique in its mineral composition. Beside very intriguing mineral lorandite (TlAsS<sub>2</sub>), there are 45 other minerals. Contaminated soils with heavy metals can potentially lead to the uptake and distribution of these metals in the edible plant parts causing risk to human and animal health. Investigations have been initiated to determine the levels of uptake and distribution of As, Sb and Tl, as well as some other heavy metals, to the different parts of the species *Thymus alsarensis*, an endemic species from this locality. Samples of different parts of the plant (root, stem, leaf and flower) and corresponding soils were processed, digested and then analyzed by atomic emission spectrometry with inductively coupled plasma (ICP-AES). It was found that the accumulation of As, Sb and Tl in this endemic species is significantly high. The percentage of As, Sb and Tl being diethylenetriaminopentaacetic acid (DTPA) extractable in soils indicated very high mobility in soil of As and Tl.

Key words: heavy metals, *Thymus alsarensis*, distribution, Allchar (Alšar), Republic of Macedonia

## EN-37

# DEVELOPMENT OF THE SUSTAINABLE WATER MANAGEMENT OF DOJRAN LAKE

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Lake Dojran belongs to the Peon group of natural Balkan lakes, a typical eutrophic lake with a complex ecosystem, characterized with significant and rich biological diversity. Dojran Lake is a part of the wider river Vardar catchment, which belongs to Aegean Sea Basin.

This paper describes Dojran Lake from ancient time and during the past years when it was drying up, towards integrated sustainable water management solution of “Project for Salvation of Dojran Lake” in 2001. Since 2002 Dojran Lake is recharged with water from Wells System in Gjavoto. According to current water level measures it will take 10 more years to achieve the minimal water depth in the lake.

Development of sustainable water management of Dojran Lake is a progress that will maintain and enhance economic opportunity and community well – being while protecting and restoring the natural environment upon which people and economies depend. Within 9 years of “Gjavoto” operation, Macedonia believes to develop a sustainable water basin within authentic biodiversity, community and tourism.

The results reached in the period of 2002 till 2011 on the quality of the water based on the physical and chemical parameters of the lake water (temperature, pH, oxygen, total phosphorus, total nitrogen) show that there were no changes on the water quality, i.e. sustainable quality of the water in the lake.

Key words: Water, Sustainable, Environment, Economic, Community

## EN-38

### METHOD DEVELOPMENT AND DETERMINATION OF PHTHALATES IN SURFACE AND GROUND WATERS IN MACEDONIA

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Phthalates are organic compounds with multiple applications in modern life. They are used as additives in mass production of plastics in order to improve their characteristics (flexibility, transparency, durability, and longevity). Also, they are used in pharmaceutical and cosmetic industry, in childrens' toys etc. Due to the increased use of plastics, large amounts of waste plastics end up in the environment.

During the degradation process of plastics, phthalates are released as a byproduct which can easily contaminate the entire environment (air, water and soil) and consequently the food which we consume. Their detrimental effect on humans has still not been sufficiently investigated. Some research papers show that they can reduce testosterone quantity, cause cancer etc. Phthalates can enter the human body through food products, water, air, pharmaceuticals and cosmetics products.

We have studied the presence of the following most commonly used phthalates in rivers, lakes and ground waters in Republic of Macedonia: benzyl butyl phthalate, dibutyl phthalate, diethyl phthalate, dimethyl phthalate, di-octyl phthalate, bis(2-ethylhexyl)phthalate. The extraction of the water samples was carried out by liquid-liquid extraction (LLE) with hexane. The phthalates in the concentrated extract were subsequently analyzed by gas chromatography – mass spectrometry (GC–MS). The GC method used was based on the US Environmental Protection Agency (EPA) method which was modified mainly in respect to the injection technique. Furthermore a comparison was made between a standard gas chromatography – quadrupole mass spectrometry (GC–QMS) and two dimensional gas chromatography – time of flight mass spectrometry (GC×GC–TOFMS).

Key words: phthalates, water, environment, GC–MS, LLE

## EN-39

### WASTE TREATMENT FROM POLYMER COMPOSITE MATERIALS

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The increased use of composites in industry continuously creates enormous amount of waste to be handled in the future. Also, for this type of materials, several regulations put pressure on producers to consider the waste treatment. Waste treatment of polymer composites is more complex compared to recycling of steel and aluminium, since they contain a mixture of materials with a multitude of combinations of fibres and polymer matrixes. In addition, for sandwich constructions there is also core material to consider.

In this paper we started with a research of the most important issues influencing the waste management of waste products and manufacturing waste containing composite materials. These issues are environmental demands in form of regulations, waste streams, techniques for material recycling, energy recovery and methods for analysing costs and environmental effects. The studied techniques for treatment of waste are focused to material recycling and energy recovery. In the framework of this paper investigations and experimental work were performed within the case studies. The case studies were divided into three groups with respect to the included materials: carbon fibre reinforced plastic, thermoset glass fibre composite - sheet moulding compound and thermoplastic composite with natural fibre. Also, analysis of the costs and environmental effects were made. The costs of the different waste treatments were analysed from a waste producer perspective. The influence of the environmental effects was studied with Life Cycle Assessment (LCA) according to the standard ISO14040. According to the results of the analysis corresponding recommendations were proposed for each material.

Key words: composites, waste treatment, recycling, energy recovery, environmental effects.

## EN-40

### QUALITATIVE ANALYSIS OF THE GALVANIC WASTE WATER

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The technological process of galvanizing after the quantitative and qualitative characteristics is a significant polluter of water. Many pollutants in the form of metal ions ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$ ...), cyanide, phosphates, acids, alkalis, fats and oils, organic solvents, surfactants and many other pollutants are released into environment. Heavy metals brought to the surface water do not decompose biologically. They are accumulated in the flora and fauna of rivers, which are due in the food chain and thus indirectly pose a major threat to human health. Based on parameters that determine the presence, quantity and characteristics of heavy metals gives an analysis and review of galvanic waste water. The parameters examined were the presence of toxic metals and their ionic forms, pH and COD. The subject of this project is discusses of the quantitative and qualitative characteristics of the waste water and provide examples of conventional and unconventional methods of their treatment.

Key words: qualitative analysis, waste water, galvanization.

## EN-41

### RISK ASSESSMENT OF INDUSTRIAL HAZARDS

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In the process of planning and certain areas and towns development, some omissions are frequently made in treating the existing natural conditions and the overburdening of the environment with technological systems. The normal functioning of these systems requires large quantities of various chemically aggressive materials.

The subject of this study is choosing an appropriate methodology of the logical tree of events for risks assessment of industrial hazard, such that it would calm the consequences of these hazards which can have unforeseeable scale. The chosen industrial plant for the risk assessment index is operation for the stocking of liquefied petroleum gas (LPG).

This method is primarily used for the industrial risk quantification and for defining one or several risk scenarios. It gives us the required information for risk assessment and for reducing the infinite possible combinations of sources, adverse events and expected damages. Such information must be both qualitative and quantitative. It must include risk sources and the related adverse events, the phenomena produced by the adverse event, and even the specific meteorological conditions and the presence of people exposed to risk in certain areas.

**Key words:** risk, industrial hazard, technological disaster, an assessment of industrial hazard

## EN-42

### DETERMINATION OF HEAVY METALS IN MILK AND DIARY PRODUCTS

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Milk and diary products are components of the daily nutrition. The input of necessary nutriments is through food; however, there is a possible risk of toxic components input in case of contamination of the raw materials or contamination during the several steps of the manufacturing or packing processes.

The aim of this paper was to determine the concentrations of some heavy metals: lead, cadmium, arsenic, zinc and copper in commercial samples of bovine milk, and eight types of diary products, using atomic absorption spectroscopy (AAS).

The results of 90 analyzed samples are presented, including 10 samples of milk and 10 samples of each of the diary products: yoghurt, white cheese, cheese spread, yellow cheese, curd, sour cream, butter and chocolate milk, from different producers from Republic of Macedonia.

The obtained results show that in two milk samples the measured concentration of lead (0.02 mg/l) is at the limit of MAC (2005), which is not the case with the other diary products. The concentration of cadmium, arsenic and copper in all of the samples of milk and diary products is bellow the former MAC (1983). From this point of view, the products are safe for consumption.

Key words: milk, diary products, heavy metals, AAS

## EN-43

# DETERMINATION OF HEAVY METALS IN THE SLUDGE OF KAMENICHKA RIVER

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This paper was motivated by the ecological disaster in 2003, when arid from the Macedonian lead and zinc mine "Sasa" spilled out into the Kamenichka river, as well as later researches on the presence of heavy metals in the sludge at the entrance of the river Kamenichka into the Kalimanci lake, and at the entrance of the Bregalnica river into the Kalimanci lake.

Within this study, determining the concentrations of some heavy metals, such as lead, zinc, copper, etc. in the samples of the sludge was done using ESA. Also, XRD method was used for performing structural analysis.

The results of the research show that the investigated area Kamenicka river is contaminated with lead nearly 70, zinc nearly 33, and copper nearly 50 times higher than the MPC of heavy metals in sludge for use in agriculture. Also, it was shown that the concentration of heavy metals in the investigated area Bregalnica river is below the limit of the MPC, except for the metal Zn with a concentration which is 20 times higher.

XRD measurements of the investigated samples show that the sludge contains Quartz-Q, Feldspat-F and Hydrosericit-Ilit-I, or Quartz-Q, Feldspat-F and Hydrosericit-Ilit-I.

**Key words:** ecological disaster, sludge, heavy metals, ESA, XRD

## EN-44

### **ANALYSIS OF SOME ENVIRONMENTAL AND ANTHROPOGENIC INDICATORS THAT INFLUENCE FISH STOCKS IN THE BLACK SEA ECOSYSTEM**

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The Black Sea fish stocks are influenced by several of human induced activities, most of them with highly negative impact on their state. In this paper, the main threats on the different categories such as local, shared, migratory, highly migratory and anadromous fish stocks were emphasized. Loss of valuable spawning and nursery habitats in rivers lagoons and modification in river flow regimes was recognized as highly negative on anadromous species (sturgeons, shad).

Loss of valuable marine habitats by silting, damping, etc., influenced negatively, especially local fish stocks of Gobiidae and red mullet. Loss of higher trophic predator species (Bonito, dolphins, etc.), algal blooms and reduction of water transparency, pollution, and introduction of alien species represent other factors affecting negatively fish stocks and their ambient. Anthropogenic pressures, such as illegal fishing and use of destructive harvest techniques, unreported and unregulated fishing activities were found to be among the major threats of fish stocks deterioration. The last but not least, is standstill of regional cooperative management of fisheries and climate changes.

Keywords: Black Sea, fish stocks, threats, deterioration, management

## EN-45

### CONTENT OF HEAVY METALS IN MEDICINAL PLANTS FROM SOUTHEAST SERBIA

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The essential and non-essential heavy metals Fe, Cu, Zn, Mn, Ni, Pb and Cd were determined in the selected medicinal plants taken from various places in pollution-free Southeast areas of Serbia. Flame AAS was used for determination of these metals.

The heavy metal concentrations (Fe, Cu, Zn, Pb, Ni ) in the examined medicinal plants are lower than permitted values recommended by the permitted standards.. The observed variation in metal contents may be connected with the climate conditions (soil and water quality) and a pollution/pollution-free degree.

The amounts of Cu, Zn and Cd are comparable, while the amount of Ni, Mn, Fe in the investigated samples differ significantly. Probably, amounts of the accumulated metals (Cu, Zn and Cd) in samples of herbs highlight a kind of predisposition of different plant species from the same area to accumulate the same quantities of the particular metal .

Cd and Mn contents in tested samples of medicinal plants from the region of Southeast Serbia are higher than permitted values for edible plants expressed as ppm of heavy metals on fresh plant, but no results for permitted values for medicinal plants. The results indicate the great importance of monitoring the content of heavy metals in medicinal herbs. This study may indicate the possibility of application of medicinal plants as bioindicators of environmental pollution. It is evident that the selected medicinal herbs from the pollution-free areas of Southeast Serbia may be safely used as an alternative medicaments and/or additional medical agents.

*Keywords:* heavy metals, medicinal herbs, pollution-free area, Southeast Serbia

## EN-46

### **EXPERIENCES IN APPLYING THE STANDARDS MKS EN ISO 9001 AND MKS EN ISO 17025 IN THE FIELD OF ENVIRONMENT AND OCCUPATIONAL SAFETY**

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Republic of Macedonia as EU Candidate country aims to harmonize national legislations in compliance with European regulations in all fields, thus as well in the field of environment and occupational health and safety. Therefore, the process of adjustment of legislation includes introduction of standards in the mentioned fields. Implemented MKS EN ISO 9001 standard in certain organization represent established system for quality management concerning services offered to the users. The term quality characterize, completion of needs and requests of clients of services, determined with agreements, information and implementation of stated requests within the international and national standards, laws and ordinances.

MKS EN ISO 17025 standard states general requirements concerning competence of Testing Laboratories, actually states conditions which must be fulfilled by the Laboratory in case if it is recognized as competent for conduction of testing, including sampling for the purpose of testing. The competence is defined as presented capability for the use of knowledge and skills, while accreditation is official confirmation of competence of the laboratories by the Institute for accreditation of the Republic of Macedonia (IARM).

The following reasons can be mentioned concerning introduction and implementation of the standards:

- Gaining greater credibility by the clients of the services,
- Improved quality of work in the laboratory and assurance of the results,
- Recognition of the results from the accredited laboratories by the clients of the services,
- Eased procedure for cooperation concerning exchanging of experiences and harmonization of procedures between accredited laboratories.

This paper presents experiences from Environmental researches laboratory of Tehnolab Ltd Skopje, since 2005 certified under Quality management system MKS EN ISO 9001, and since 2008 accredited by the Institute for accreditation of the Republic of Macedonia under MKS EN ISO 17025.

Gained competences of Tehnolab due to the introduced and implemented standards are the following:

- Great work organization, management and control of all types of documents, use of measures for improvement of the efficiency of the quality management system MKS EN ISO 9001
- Ensured competence of the Environmental researches laboratory due to qualified and highly educated experts, work conditions (relevant space for the researches), use of recognized standardised research methods, relevant calibrated equipment for performance of the researches according MKS EN ISO 17025.

The Laboratory confirms it's competence throught:

- Assurance of measurement folow up accompanised with regular calibration of the equipement and
- Participation in comparative measurements between accredited laboratories

Key words: quality system, competence, calibrated equipment,

**INORGANIC CHEMISTRY AND TECHNOLOGY (I)**

I - 1

**STRUCTURE AND MORPHOLOGY OF CERAMICS  
FROM PRETREATED MSWA**

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The phase composition and the structure of six new ceramics, obtained by mixing two kinds of pretreated bottom ashes from municipal solid waste incinerator (MSWA) and three different industrial clays were studied in details. The open and closed porosity were evaluated by water absorption and density pycnometric measurements with gas pycnometer. The phase compositions and the amounts of formed crystal as well as amorphous phases were estimated by XRD analysis. Finally, the structures of obtained samples (both surface and fractures) and the morphology of formed crystal phases have been characterized with SEM coupled with EDS. The results elucidate that the samples are characterised with low open (1-4 vol%) and high closed (10-17 vol%) porosities and an untypical for traditional ceramics phase composition, based on anorthite s.s., pyroxene and some residual quartz. It is also demonstrated that the main structure of the new materials is based on tiny anorthite crystals, sized between 3 and 10  $\mu\text{m}$ .

Key words: industrial wastes, ceramics, structure, phase composition.

I - 2

**CRYSTALLIZATION BEHAVIOUR AND MICROSTRUCTURE OF THE  
GLASS-CERAMICS FROM THE SYSTEM  $\text{Na}_2\text{O}/\text{TiO}_2/\text{BaO}/\text{B}_2\text{O}_3/\text{Fe}_2\text{O}_3$**

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The interest in glass-ceramics with high concentrations of 3d-transition metal ions is determined by their electrical and magnetic properties and the possibility to combine them and to obtain multiferroic materials. Due to their magnetoelectric properties, multiferroics find application, depending on the size and type of the formed crystals, in microelectronics, spintronics, sensor technology and for energy storage.

The present work reports on the synthesis, phase formation and microstructure of the glass-ceramics, obtained from the system  $\text{Na}_2\text{O}/\text{TiO}_2/\text{BaO}/\text{B}_2\text{O}_3/\text{Fe}_2\text{O}_3$ . The characteristic temperatures of the samples were determined by differential thermal analysis. X-ray diffraction was used for phase identification. Scanning electron microscopy, combined with energy dispersive x-ray analysis, was utilized for microstructural characterization and determination of the elemental composition of the formed crystals. The carried out investigation of the crystals shows presence of compound  $\text{BaTiFeO}_3$  needle-like crystals together with tiny magnetic crystals for the slowly cooled melts. For the specimens, obtained by quenching the melt, only formation of small magnetic crystals with average size of some ten nm was observed. The annealing of the fast cooled samples above the glass-transition temperature results in further growth of the tiny crystals up to some  $\mu\text{m}$ .

Key words: barium titanate, iron oxide, crystallization, multiferroics

### I-3

## EVALUATION OF EXCAVATION RAW MATERIALS AND RESPECTIVE RAW MIXES

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The scope of this study is to investigate the possibility of using the raw materials - derived from the excavations during the new cement plant construction in Albania - in the raw mix production. These raw materials were categorized into three different groups depending on their mineralogical and chemical characteristics. The selected clay, limestone and mixed samples of excavation materials from the area of Burizane have been analyzed with the methods: X-Ray Fluorescence and Wet Chemical Analysis. Based on their chemical analysis, it was concluded that clay and mixed materials were inhomogeneous. On the contrary, limestone materials were found to be almost homogenous. Using the above materials without any silica source cannot lead to raw mix with acceptable indexes Lime Saturation Factor (LSF), Silica Modulus (SIM) and Alumina Modulus (ALM). The excavation clay is a relatively inhomogeneous material, with both SiO<sub>2</sub> and CaO standard deviations being quite high (9.92 and 6.38 respectively). There are significant quality differences between the excavation materials and the materials from the flysch quarry of Burizane. The silica modulus of excavation materials is 1.78 compared to the quarry's 4.32. The limestone rock is a nearly pure limestone apart from four samples which had high amount of silicon oxides (12-24%). The analyses of the excavation limestone samples showed high similarity with the respective analyses of limestone from the Burizane quarry. The mixed materials were inhomogeneous material with high values of standard deviations in the SiO<sub>2</sub> (9.42) and CaO (9.99) contents. It is not possible to produce a raw mix confronting with the set LSF, SIM and ALM targets, without using a siliceous corrective material. The silica materials participation can fluctuate between 5.9% and 7.5% depending on the SIM target. Because of the excavation's material low silica modulus, there is no need of bauxite or iron source. These materials could be used for the raw mix production replacing the bauxite as long as the flysch quarry exploitation is permissible. The consumption of these materials is expected to quickly diminish the size of the deposit.

Key words: Limestone, Flysch, Bauxite, Iron Source, Raw Mix.

## I-4

## MODIFIED ZEOLITE / ROCK PHOSPHATE – NATURAL MINERAL FERTILIZERS

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In the past twenty years Serbia has faced with major problems in the fertilizers production, through the reduction of national capacity, focused on fertilizer importing, consumption reducing (in yield per hectare) and generally, in agricultural production share decline in GDP. The current average use of fertilizer is below 80 kg / ha which is three times less than in other agricultural countries and third of the use in Serbia before 1990. So, it can be concluded why the production of many cultivated plants is on low profitability range. One way of overcoming this problem is the development of new natural fertilizers based on domestic raw materials, phosphate and modified zeolite, as economically cost-effective and environmentally better type than industry fertilizers, which was the subject of our research. The use of raw phosphate as fertilizer is known in practice, as economical and environmentally suited but with limited applications only on acidic soil types. The use of natural zeolite overcomes this constriction, offering the application of natural phosphates in wider range of soil types.

The starting hypotheses is that the surfactant modified zeolite with ammonium cation, increases the solubility of phosphate rock (PR) with cation exchange  $\text{Ca}^{2+}$  and  $(\text{NH}_4^+)$ , according to equation no. 1



The exchange sites vacated by  $\text{NH}_4^+$  are occupied by  $\text{Ca}^{2+}$  inducing dissolution of PR and release of P into solution. Thus, the release of P will occur at a rate determined by the rate of plant  $\text{NH}_4^+$  uptake, with P release increasing with plant growth. In the study used in this work, the following rows were used: a natural phosphate (16.43%  $\text{P}_2\text{O}_5$ ) and its concentrate (34.95%  $\text{P}_2\text{O}_5$ ) from the locality "Lisina" Bosilegrad, and zeolite from locality „Igroš“(KIK 139,0 mmol  $\text{M}^+$ /100 g), modified with  $\text{NH}_4\text{Cl}$ . Weight relationship modified zeolite and PR was 5:1 in the aquatic system and the parameters monitored was pH, conductivity, free calcium and phosphorus. Results indicated that the surfactant modified zeolite has increased the solubility of phosphorus from 1.56 to 3.62  $\text{mg l}^{-1}$ , reducing the content of free calcium from 28 to 2.4  $\text{mg l}^{-1}$  in the same time. Verification system will be done through the vegetation experiments, which are currently being created.

Key words: mineral fertilizers, surfactant modified zeolite, natural phosphates, cation exchange

I-5

**EXAMINING THE POSSIBLE USE OF NATURAL RAW MATERIAL  
"TREPTEL"-BITOLA FOR THE SYNTHESIS OF ZEOLITE TYPE 4A**

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Zeolites have wide field of applications because of their specific structure and characteristics. Republic of Macedonia is rich with natural non-metallic raw materials that are very clean, without colored impurities. Also, according to the chemical composition there are components necessary for the synthesis of zeolites. "Trepel" from Bitola, Republic of Macedonia was used as a natural raw material for low temperature synthesis of zeolites. The synthesis was accomplished using the following molar ratios of oxides:  $\text{SiO}_2/\text{Al}_2\text{O}_3=1.3$ ;  $\text{Na}_2\text{O}/\text{SiO}_2=3$ ;  $\text{H}_2\text{O}/\text{Na}_2\text{O}=50$ , characteristic for zeolite type 4A.

The chemical composition of the resulting mixture was:  $3.9 \text{ Na}_2\text{O} \cdot 1.3 \text{ SiO}_2 \cdot 195 \text{ H}_2\text{O}$ .

Additional amounts of  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  components were added by  $\text{NaAlO}_2$  and  $\text{NaOH}$ . The gel was obtained by crystallization of the mixture for 24 hours at room temperature. After the synthesis (2, 4 and 6 hours), the obtained products were examined by chemical, structural and thermal methods. The results of structural investigations confirmed that the obtained zeolite was of type 4A. The same conclusions was confirmed by IR-method. The research will continue in the future and the synthesized zeolite will be tested for application in catalytic reactions and ion exchange.

Key words: raw material, zeolite, synthesis, IR-method

**I-6**

**FABRICATION OF COAL ASH CERAMICS  
CASE STUDY: OPTIMIZATION OF MAIN PROCESS PARAMETERS**

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Fly ash is one of the by-products generated in the coal burning power plants. According to the morphological characteristics, physical and chemical properties fly ash has potential use in ceramic fabrication. Fly ash from the forth zone of electrostatic precipitator from the power plant REK Bitola, Republic of Macedonia was used in this case study.

Optimization of the consolidation process parameters for fabrication of dense ceramics was the aim of the study. The optimization was conducted on the main process parameters (pressing pressure, sintering temperature and heating rate) and their interactions on the properties of the fabricated dense ceramics (porosity and bending strength). The optimization was performed applying the 3D surface model and the obtained results were presented in the graphical and analytical form. “Statgraphics Centurion” software package was used for this purpose.

Key words: optimization, consolidation, process parameters, fly ash, ceramics

I-7

## LOW TEMPERATURE SYNTHESIS OF ZEOLITE 4A FROM NATURAL RAW MATERIAL "PEMZA "

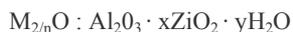
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Zeolites are the crystals with defined structure and determined geometry of pores. The general composition of zeolites is presented with the following formula:



Zeolite type 4A from natural raw material "Pemza" was synthesized in this research. The low temperature synthesis was performed from 363 K to 373 K, where the time of reaction was 2, 4 and 6 hours. The gel was obtained during 24 hours at room temperature. The chemical composition of the natural raw material "Pemza" is: 70% SiO<sub>2</sub>, 13% Al<sub>2</sub>O<sub>3</sub>, 7% Na<sub>2</sub>O and presents the base for the synthesis of zeolite type 4A.

The synthesized zeolite 4A was characterized by X-ray diffraction, IR-method and thermal methods.

The results from the applied characterization methods confirmed the structure of the zeolite type 4A.

Key words: zeolite 4A, synthesis, "Pemza", IR - method

I-8

**COMPARISON OF DIFFERENT COLORIMETRIC METHODS FOR  
DETERMINATION OF TOTAL PHOSPHORUS IN SOILS**

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The most widely used method for determination of total phosphorus in soils is perchloric acid digestion, which is a recognized standard. The first part of this study compares an alternative digestion method, using aqua regia (ISO 11466 and EPA Method 3052) and HF + HClO<sub>4</sub>, with perchloric acid digestion procedure, and also compares two methods for the measurement of P on the basis of five internationally certified standard soils and 20 real-life soils with widely different extractability of phosphorus. The total phosphorus in soil extracts was measured colourimetrically after neutralization of the digests to pH 3 ± 0.5 by two widely spread methods – (i) method of Murphy and Riley and (ii) Phosphate test Spectroquant (Merck KGaA), using Boeco S-22 UV/VIS Spectrophotometer and Spectroquant Pharo 100 spectrometer respectively. The relationships between methods are examined statistically.

A good agreement of the results from ISO 11466 and EPA Method 3052 was established for all certified samples. The microwave aqua regia method was comparable, both in precision and accuracy, with the hot plate aqua regia method. The phosphorous amount found with the HF + HClO<sub>4</sub> digestion method was in good agreement with the certified mean values while the superiority in extracting phosphorus, when compared to other methods, was obvious.

The method suggested by Merck KGaA has significant advantages. They are mainly related to rapidity and ease of determination. However, in this case, significant dilution of samples shall be required (dilution factor over 2000), which may considerably affect the measurement accuracy.

Keywords: phosphorus determination, Murphy and Riley, Phosphate test Spectroquant

I-9

## **CORUNDUM COMPOSITE CERAMICS AS A SUBSTRATE MATERIAL FOR DEPOSITION OF VITREOUS CARBON**

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The ceramics consisting of more than 95 %  $\text{Al}_2\text{O}_3$  is called corundum ceramics. The name comes from the name of the  $\alpha$ -crystalline form of the aluminum oxide - corundum.

The ceramic material on  $\text{Al}_2\text{O}_3$  basis is bio-inert, non-toxic, non-allergic and non-carcinogenic material and for that reason it is frequently used as material for orthopedic and dental implants. Unfortunately it is chemically inert in the human body and cannot form the biological bond with the bone tissues. To overcome the problem we applied biocompatible vitreous carbon coating. We studied the physico-mechanical and microstructural properties of the  $\text{Al}_2\text{O}_3$  ceramics, used as substrate for the biocompatible polymer matrix material. We used calcium titanate as a modifying agent with the aim to increase the mechanical properties of the composite material and to reduce the sintering temperature. At the same time this additive enhances the preparation of the vitreous carbon coating.

The compressive strength is more than 2000 MPa and the flexural strength is more than 200 MPa. The morphology of the composite material  $\text{Al}_2\text{O}_3$  - vitreous carbon was studied by scanning microscopy. The obtained results show that the chemical composition and the technological parameters favor the formation of sufficiently strong bond between the composite material and vitreous carbon coating.

Key words: corundum, vitreous carbon, alumina, orthopedic implant,

I-10

## PHOTOINDUCED CHANGES IN OPTICAL BAND GAP OF GALLIUM CONTAINING TELLURIDE THIN FILMS

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Amorphous chalcogenide materials possess a unique property of being transparent in the infrared region of the spectrum, which make them promising materials for IR optics. Under action of light, the chalcogenides exhibit many photoinduced phenomena as a result of the glass structure changes, leading to red or blue shifts of the optical absorption edge.

The addition of third component to chalcogenide matrix complicates the atomic structure of the glasses and leads to modification in the optical behaviors of the material.

We deposited Ge-Te-Ga thin films by vacuum evaporation on glass substrates from the initial bulk synthesized materials.

The structure of the deposited films was investigated by X-ray diffraction technique and transmission electron microscopy. Additionally, Auger Electron Spectroscopy was applied in order to verify the film composition.

Photoinduced changes were realized by exposure of the films with a halogen lamp illumination. The transmission spectra of the thin films were measured before and after irradiation, and the optical band gap was derived from the spectra using the Tauc procedure.

The photoinduced changes in the optical gap (E<sub>g</sub>) of Ge-Te-Ga films were investigated and discussed in terms of the local ordering modification due to Ga incorporation.

Keywords: Chalcogenide glasses, thin films, photoinduced changes

I-11

**CHARACTERIZATION OF NATURAL AMORPHOUS SiO<sub>2</sub>  
FROM A NEW DEPOSITS IN THE REPUBLIC OF MACEDONIA**

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Amorphous SiO<sub>2</sub> is one of the most intensively examined raw materials in the materials science, with a broad use in various industries. It is applicable in ceramic, chemical, pharmaceutical, food industries, in the drinking and waste water treatments, as well as in new technologies for production of semiconductors, optical fibers, solar cells etc. For the characterization of natural amorphous SiO<sub>2</sub> found in the deposit near the village of Rozden, Kavadarci, there has been conducted physical-mechanic, chemical, mineralogical, SEM, IR and thermal examinations. Physical-mechanic analysis have shown that it is a white to grey colored rock, of low hardness (compressive strength of 3,5 – 4,5 MPa), a low volumetric mass (0,55 – 0,60 g/cm<sup>3</sup>) and high porosity (73 – 75%). Chemical analysis has shown that the material contains over 90 % of SiO<sub>2</sub>, and from a chemical point of view it presents a high quality amorphous raw material, suitable for various uses. Mineralogical analysis has shown a high percentage of isotropic mass content, with minimal contents of submicroscopic cryptocrystalline mass. Thermal analysis has shown that the material does not crystallize after a thermal treatment at 1000 °C, i.e. it remains amorphous material, which shows high thermal stability. Based on the conducted research of the raw material from the new deposit, it can be concluded that it presents SiO<sub>2</sub>-diatomite of high quality, useful for various purposes.

Key words: amorphous SiO<sub>2</sub>, diatomite, characterization

I-12

**ADSORPTION CHARACTERISTICS OF SYNTHETIC ZEOLITES  
CaNaX AND MgNaX DETERMINED FROM THE WATER VAPOR  
ADSORPTION ISOTHERMS**

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The adsorption of water vapor on synthetic poly-cationic zeolites CaNaX and MgNaX was investigated by static gravimetric method. Adsorption equilibrium of water vapor on zeolites has been defined by varying the operation parameters:  $T=298\text{K}/P=0.536\text{-}7.906\text{ hPa}$  and  $T=308\text{K}/P=1.085\text{-}14.440\text{ hPa}$ . The as-obtained experimental data were successfully correlated applying the linear forms of n-BET equation and equation of Dubinin-Radushkevich. The remarkable good fit of the experimental equilibrium data to the used equations was evident from the linearity of the curves and the high values of correlation coefficients. Statistic number of adsorbed molecular layers, monolayer capacity, specific surface, isosteric heat of adsorption and volume of pores of zeolites were evaluated. Both zeolites have excellent adsorption capacities for water vapor at investigated pressures. The determined characteristic values correspond to the structure of the zeolites and can be used for selection of zeolites in adsorption processes and processes of heterogeneous catalysis.

Key words: adsorption, synthetic zeolites, water vapour

I-13

## THERMAL TRANSFORMATIONS OF THE ZEOLITE 4A OBTAINED BY FLY ASH

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The zeolite type 4A was obtained from fly ash. The high content of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the fly ash makes it a convenient raw material for the synthesis of the zeolite type 4A. Zeolites are useful materials widely applied as adsorbents, molecular sieve and catalysts. Cavities in zeolite structures are full of water which is known as zeolite water.

The DTA curve of the synthesized zeolite 4A displayed an enormous endothermic effect, which was a result of the zeolite water. The zeolite structure was transformed at 648 K into nepheline, followed by  $\beta$  carnegierite and the final exothermic effect was a result of the crystal phase –  $\beta$  cristobalite. The weight of ignition was determined from the TG curve and it was 20 wt.%.

Key words: fly ash, zeolite type 4A, thermal analysis

**I-14**

## **SYNTHESIS OF INORGANIC BINDER WITH TECHNICAL PROPERTIES**

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Inorganic aluminosilicate binders based on sodium and potassium silica solution with schistous clay dust were synthesized under addition of different fine filler materials. The aim of this study is research and development of aluminosilicate composite material with technical properties. From this point of view compressive and flexural strengths of the final composites with specific particle-size distribution (PSD) were investigated. PSD method was determined by standard sieve analysis. Alkaline activation reactions for pure aluminosilicate matrix were described by using thermal analysis. The processes of disaggregation and the following severance of Me-O bonds, forming of coagulated structures and sequent polycondensation were systematically studied by means of differential scanning calorimetry (DSC). Final modifications of inorganic aluminosilicate composites were based on standard impregnation methods of concrete cements. Resulting properties were investigated with regard to the type of admixture (organic polymers, alkali metals solutions), setting time and potentialities of atomic diffusion to fill up molecular sieve.

Key words: Inorganic polymer, Compressive and flexural strengths, DSC, Impregnation

I-15

**HYDROTHERMAL REACTION BETWEEN  
FLY ASH AND CALCIUM HYDROXIDE AT 100 - 130 °C**

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The objective of this research was to utilize fly ash from coal fired power plant in Oslomej, Kicevo in order to produce lightweight building materials. The fly ash from Oslomej is a typical class F (low calcia) fly ash, with 6.11 % CaO. X-ray and microscopic analysis of the investigated fly ash have shown that the glass phase represents a quantitatively predominant component. The fly ash is a suitable starting material for production of lime-fly ash bricks which require a minimum of preliminary processing, such as grinding or milling. Lime-fly ash bricks are a variety of lime-sand bricks, but differ by a lower bulk density and better heat insulating properties, since heavy quartz sand is replaced by lightweight fly ash. Lime-fly ash bricks have been prepared from 58% fly ash, 17% Ca(OH)<sub>2</sub> and 25% H<sub>2</sub>O. The testing bricks have been steamed in an autoclave at temperature of 100, 110, 120 and 130 °C. The obtained products have shown a bulk density of 780 - 800 kg/m<sup>3</sup> and compressive strength of 2.5 - 4.0 MPa. X-ray powder diffraction analyses have shown that during the hydrothermal treatment of the samples the following new minerals were formed: CSH, C<sub>2</sub>SH, tobermorite and katoite.

Keywords: hydrothermal reaction, fly ash, calcium hydroxide, compressive strength.

I-16

## DESIGN OF POZZOLANIC MORTARS BASED ON DOMESTIC CLAY MATERIALS

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The protection of cultural heritage objects demands the application of materials whose properties must be compatible with the historical materials. The results in the field of protection and conservation of immovable objects of cultural heritage in Serbia are mainly the result of the work of enthusiasts. Evidently, this is not sufficient in order to develop materials with adequate characteristics for use in future restoration processes.

One of the main problems of immovable cultural and historical monuments protection and restoration is the selection of appropriate mortar. The compatibility of new designed mortars should reflect appropriate textural, mechanical and microstructural correlation with the original ones. The examination of historical mortars provides the data of their composition and specific properties which represent the foundation of new and adequate mortar composition for restoration process.

The aim of this study was to investigate the properties of two types of domestic clay materials required for designing appropriate lime mortar mixtures in order to perform the restoration of the immovable objects of cultural heritage. Their properties were compared with two types of commercially produced materials previously used in the field of the restoration and conservation of the objects of cultural heritage. The characterization of the raw materials was performed by chemical analyses, XRD, DTA/TG and DSC analysis. Pozzolan activity quantification was performed by the standard flexural strength and conductometric mortar mixtures characterization, but new methods based on spectrophotometric and volumetric measurements were developed. These methods are based on the measurements of the consumption of calcium ions in the  $\text{Ca}(\text{OH})_2$  aqueous solutions of the examined clay materials. Porosity reduction, enhancement of the hydration process (formation of C-S-H mineral phase) and carbonization process were noticed based on SEM investigation. The design of pozzolanic mortars based on domestic clays presents a significant step toward solving the problem of the restoration of cultural and historical monuments.

Keywords: Cultural heritage, materials characterization, pozzolan activity, pozzolan mortars

I-17

## PHYSICO-CHEMICAL PROPERTIES OF GLASSES FROM THE $\text{GeSe}_2\text{-Sb}_2\text{Se}_3\text{-PbSb}_2\text{Te}_4$ SYSTEM

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Multicomponent chalcogenide glassy (ChG) semiconductors in which as initial components chemical compounds are used instead of chemical elements guarantee on one side the obtaining of wider glass-forming regions and on the other more defined composition and structure, and as a result wider spectrum of their applications. Especially, the interest towards the Pb-containing ChG is provoked by their hutch usage as functional materials for sensors production.

In these reasons our attention was attracted on synthesis and characterization of glasses from the multicomponent  $\text{GeSe}_2\text{-Sb}_2\text{Se}_3\text{-PbSb}_2\text{Te}_4$  system. The glass-forming region in this pseudo-ternary system is situated in the  $\text{GeSe}_2$ -rich region and lies partially on the  $\text{GeSe}_2\text{-Sb}_2\text{Se}_3$  (from 0 to 70 %  $\text{Sb}_2\text{Se}_3$ ) and  $\text{GeSe}_2\text{-PbSb}_2\text{Te}_4$  (from 0 to 27 mol %  $\text{PbSb}_2\text{Te}_4$ ) sides of the Gibbs' concentration triangle. No glasses were obtained in the binary  $\text{Sb}_2\text{Se}_3\text{-PbSb}_2\text{Te}_4$  system.

The temperatures of crystallization ( $T_{cr}$ ) and melting ( $T_m$ ) of glassy samples were determined by differential thermal analysis and were established to vary from 340 to 446 °C and from 390 to 620 °C, respectively. Two exothermal effects of crystallization were registered for the  $(\text{GeSe}_2)_{45}(\text{Sb}_2\text{Se}_3)_{45}(\text{PbSb}_2\text{Te}_4)_{10}$  composition, while for other samples the crystallization of one phase was observed. Two endothermal effects related to  $T_m$  appeared on the thermograms. The low-temperature effects are related to the formation of solid solutions of  $\text{Sb}_2\text{TeSe}_2$  with  $\text{GeSe}_2$  and  $\text{Sb}_2\text{Se}_3$ , while the compositional dependence of the higher thermal effects proves indirectly the existence of an eutectic in the concentration area around the  $(\text{GeSe}_2)_{63}(\text{Sb}_2\text{Se}_3)_{27}(\text{PbSb}_2\text{Te}_4)_{10}$  composition

The density of the investigated glasses was measured from 4.74 to 5.26 g/cm<sup>3</sup> depending on their composition. The compactness and Hruby's criterion were calculated. A correlation between the investigated properties and the samples composition was determined. When the concentration of the  $\text{SbSe}_{3/2}$  structural units increases at the expense of  $\text{GeSe}_{4/2}$  tetrahedrons, the compactness depends on the bonds tearing and the changes in the micro-voids volume due to the introduction of higher number of atoms with bigger radii.

Key words: chalcogenide glassy (ChG) semiconductors,  $\text{GeSe}_2\text{-Sb}_2\text{Se}_3\text{-PbSb}_2\text{Te}_4$  system.

## I-18

## INVESTIGATION OF USED GRIT CEMENT STABILIZATION FOR SAFE DISPOSAL

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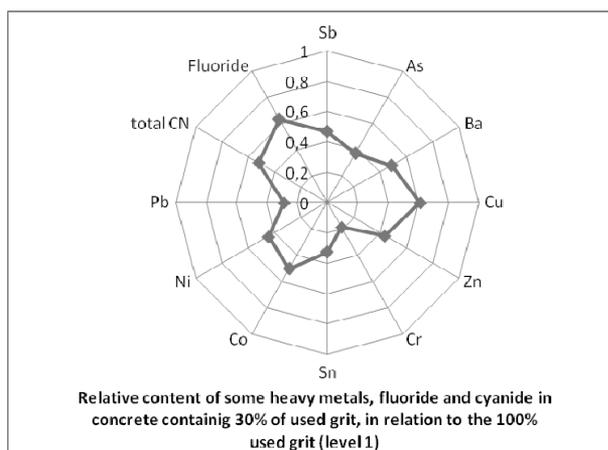
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Generated waste is possible to stabilize to become safe for disposal, but if the different stabilizing agents are used, the products based on the waste can then be used in the construction industry for the production of concrete. Stabilizing agents may be cement, white cement, dust from lime pit, lime, ash, silicates and many others. However, the most widely used stabilizer is cement, while other agents are used to replace part of cement and have a positive or negative effect on strength, precipitation and moisture. Strength is often used as an indicator of stabilization. Stabilized waste has significantly higher strength compared to unstable ones. Yield strength of stable waste is 0.35 MPa and it represents the minimum strength of waste for its safe disposal. Cement content usually varies from 5-20%, but increasing cement content leads to a better coating of individual particles of waste. Even a small amount of added cement, although not completely coat the particles of waste, leads to the occurrence of condensation and increases the hardness of waste. It is assumed that the reason this process of physical changes is caused by hydration despite the false mechanism of densification, ie. precipitation of salts such as gypsum, which further affects the strength. Strength of the material also affects the type and quantity of constituents forming the pore structure. After curing, the material density increases, which is a positive economic effect if you are thinking about disposal in landfills. However, deposition of material from the economic as such a negative, requiring capital investment, to find opportunities for further implementation of waste represents a significant economic savings.

This work includes different mechanical and chemical tests of some cement-solidificated grit samples (from 5% up to 50% of used grit content), including the TCLP and EP extract (neutral) tests, with particular attention to some heavy metals and polyaromatic hydrocarbons.



Keywords: waste stabilization, grit, heavy metals, polyaromatic hydrocarbons

## I-19

### THE ROLE OF *ALTERNATIVE FUELS* IN CEMENT PRODUCTION

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The cement industry is recognised to be responsible in managing the environmental impact associated with the manufacture of its products. Over the past 20 years specific energy consumption has been reduced by about 30%, equivalent to more than 10 million tonnes of coal per year. The use of alternative fuels today substitutes more than 2.5 million tonnes of coal every year in CEMBURAEU countries.

Dust emissions have been reduced by 90% as the industry has invested heavily in various emission abatement techniques.

Co-processing of wastes does not conflict with the waste hierarchy, as it can be classified as a technology for energy and material recovery (EU 98/2008 directive).

The cement industry is able to use waste as alternative fuels and raw materials to reinforce its competitiveness and at the same time contribute to solutions to some of society's waste problems in a way which valorises the waste and is beneficial to the environment.

The use of waste as alternative fuels in the cement industry has numerous environmental benefits such as:

- reduces the use of non-renewable fossil fuels such as coal as well as the environmental impacts associated with coal mining.
- contributes towards a lowering of emissions such as greenhouse gases by replacing the use of fossil fuels with materials that would otherwise have to be incinerated with corresponding emissions and final residues.
- maximizes the recovery of energy from waste. All the energy is used directly in the kiln for clinker production. It also maximizes the recovery of the non-combustible part of the waste and eliminates the need for disposal of slag or ash, as the inorganic part substitutes raw material in the cement.

The use of waste as alternative fuels is a safe way of valorizing waste. The organic constituents are completely destroyed due to the high temperatures, long residence time and oxidizing conditions in a cement kiln. The inorganic constituents combine with the raw materials in the kiln and leave the process as part of the clinker. Heavy metals in the cement end up bound in the concrete.

Concrete made from cement manufactured using alternative fuels has the same construction and environmental properties as concrete made from cement manufactured using fossil fuels.

Keywords: waste, alternative fuels, energy and material recovery

I-20

## NEW SPECIAL CEMENT FOR THE MAJOR HYDRO-ELECTRIC PLANT ON THE RIVER TRESKA, MACEDONIA

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The cement producer USJE - Skopje, participates in the infrastructural project for the construction of the new Hydroelectric Power Plant on the river Treska, Macedonia. The dam is double arch 64 m high with the crest length and crest level of 118 m and 364 m ASL, respectively. The volume of the estimated concrete for this purpose is approximately 30.000 m<sup>3</sup>.

In order to comply with the requirements of the new power Plant, USJE developed cement with low clinker content and low heat of hidration. In the past 3-4 years the cement was designed by varying the content of the minerals that produce heat during hidration. Natural pozzolana was used for this purpose and the strict quality control of the final cement composition was applied. The new fabricated cement was controlled on laboratory and industrial level and the final product presents pozzolana cement that complies with the both local and European standards. The increased content of pozzolans and the subsequent decreased content of clinker influenced positively the concrete durability, which is in accordance with the technical specifications of the project.

Additional tests of the cement were carried out upon investor's requirement in VDZ Germany and in ZAG Slovenia. The heat of hydration for the cements produced in 2010 and 2011 is within values of 213 – 251 J/g on 7 days (determined according to EN 196-8).

XRD semi-quantitative analyses of raw materials have been performed in R&D and Quality Department in Athens. C<sub>3</sub>A content in clinker according to the XRD analysis is in the range of 8.5-9.5 %. The amorphous phase of pozzolanas is in the range 63 to 65%.

The new product of USJE is considered as environmentally friendly cement which will be used in the framework of the major Power generation projects which is planned to be constructed in our country in the next year. The new “green” cement produced in USJE is in accordance with the sustainability efforts of the factory. The civil engineering construction of the dam is 98 % completed.

Key words : Dam.LH Cement, Environmentally friendly;

I-21

**ACTIVATION OF POZZOLANIC ACTIVITY OF KAOLINITE CLAY:  
THERMAL AND MECHANOCHEMICAL TREATMENT**

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This paper compares the pozzolanic activity of metakaolin obtained by thermal treatment and amorphous kaolin obtained by mechanochemical treatment. Optimal thermal treatment parameters are temperature 650 °C and heating time 120 min during which pozzolanic activity of 0.45 g Ca(OH)<sub>2</sub>/g Pozz is obtained. To increase activity metakaolin was milled 5 min after which pozzolanic activity rose to 0.70. Mechanochemical treatment was performed in a Herzog oscillating mill for 15–120 min. The highest pozzolanic activity of 0.74 was obtained by milling clay for 2 h.

The starting material used is Serbian kaolinite clay „Miličnica“ which is by means of kaolinite content and loss of ignition medium-quality raw material. Beside kaolinite, the other main mineral constituent is quartz. According to Aparicio-Gala'n-Ferrell - AGFI s method the clay is of medium degree of orderness.

The results indicates that both processes might be applied for obtaining reactive pozzolana from investigated kaolinite clay. It is evident that applied mechanochemical treatment results in higher value for pozzolanic activity, comparable with those obtained for commercial metakaolin. The use of mechanochemical treatment have additional benefits, applied technology is favourable in the view of environmental protection, and through the lower production cost.

Key words: metakaolin, amorphous kaolin, calcination, mechanochemical treatment, pozzolanic activity.

**METALLURGY (M)**

**M - 1**

**DETERMINATION OF THE HYDROGEN DIFFUSION COEFFICIENT IN  
TITANIUM AND ITS ALLOYS**

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The diffusion of hydrogen in titanium and its alloys was studied. The specimens in form of thin plates were hydrogenated at different hydrogen pressures and temperatures, thus, ensuring different initial concentrations of hydrogen in the specimens. The experiments were carried out in a custom made setup which allowed precursory hydrogenation of the specimens and measurement of the released gas flux during the diffusion experiments.

A diffusion model, combining the released gas flux from the specimens with the gas diffusion coefficient in the plates, was used. The experiments for determination of the hydrogen diffusion in titanium and its alloys were carried out at different temperatures, thus allowing the dependence between diffusion coefficient and temperature to be determined.

The measured values of diffusion coefficients are in good agreement with the available experimental data published by other authors.

Key words: titanium, titanium alloys, hydrogen diffusion.

**M - 2**

**MODELING THE COMPOSITION AND PROPERTIES OF STEELS  
INTENDED FOR AUTOMOTIVE INDUSTRY**

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The requirements of automotive industry toward the used steel are continually becoming more stringent. While the required strength of the steels for general use is in the range 440-590 MPa, the required tensile strength for the steel used for manufacturing components or parts of automobiles is in the range 980-1180 MPa.

This paper presents a modern method for optimizing the steel properties. Database for 92 steels was used for establishing the connection between chemical composition and mechanical properties. The chemical composition of the steel is optimized by using regression models and models with artificial neural networks. Steel with optimized chemical composition was produced.

The produced steel is subjected to chemical analysis and mechanical tests. The tensile strength and relative elongation are determined. Based on these data, the composition of the steel was optimized.

Key words: steel, automotive industry, mechanical properties, regression models, artificial neural networks.

### M-3

## X-RAY, DTA AND TGA STUDY OF ZINC SULFIDE CONCENTRATES

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The two zinc plants in Bulgaria (KCM S.A., Plovdiv and LZC S.A., Kardjali) deliver the necessary raw materials from Bulgaria and abroad. One of the main suppliers of zinc concentrates from the Balkan countries is Macedonia. The contemporary zinc production is characterized by concentrates differing in their chemical, mineralogical, phase and granulometric content. In this connection an analysis of the delivered sulfide zinc concentrates (Bulgarian and Macedonian) was made through statistical processing of data about their chemical content.

For the purpose of treating the concentrates according to the classical hydrometallurgical scheme studies were carried out using sieve, X-ray phase analysis, DTA and TGA.

Using an X-ray phase analysis of the concentrates, it was established that the following phases are present:  $\beta$ -ZnS; nZnS.mFeS; CuFeS<sub>2</sub>; PbS; SiO<sub>2</sub> ( $\alpha$ -quartz). The phase  $\beta$ -ZnS is present in all concentrates and the other established phases are represented differently in the separate concentrates.

The behavior of the concentrates during thermal treatment up to 1000 °C in air atmosphere was examined by DTA and TGA. The types and the temperature intervals of the observed oxidizing and dissociation processes were established.

The calculations made using the developed Web-based information system have shown that when the concentrates are appropriately proportioned a mix with a very good chemical composition is obtained. This leads to a stable regime of oxidized roasting in a fluidized bed furnace, which conforms to the technological requirements of the zinc hydrometallurgical technological scheme.

Key words: Zinc concentrates, X-ray analysis, DTA, TGA, charge calculation

**M-4**

**COMBINED METALLOGRAPHIC AND EDDY CURRENTS  
INVESTIGATION OF THE DEPTH OF CARBURIZED AND HARDENED  
CASES**

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Case hardening is a basic method for improvement of wear resistance and fatigue strength of parts under dynamic and thermal stresses. The characteristics of case hardening are primarily determined by surface hardness, the effective hardness depth, and the depth profile of residual stress. Case hardness depth or the thickness of the hardened layer is an essential quality characteristic of the carburizing and case hardening process. In practice the quality of carburizing process could only be evaluated by using of destructive testing methods which take a lot of time for specimens preparation and investigation process. In addition for this determination the NDT methods give an excellent opportunity for optimization of investigation process. The aim of this report is to present the experience on determination of case depth of gas carburized parts by comparison of data from light microscopy, microhardness testing and eddy currents investigation.

Key words: carburized cases, light microscopy, microhardness testing, eddy currents testing

**M-5**

**METALLOGRAPHIC INVESTIGATION OF COLD-WORK HIGH-  
CHROMIUM TOOL STEEL MODIFIED WITH NANO-SIZED SILICON  
NITRIDE AFTER HIGH TEMPERATURE QUENCHING AND TEMPERING**

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The final properties of tools are formed by heat treatment which assures the formation of microstructures capable of withstand the high loading conditions during the exploitation of the tool. High temperature quenching followed by two or three times tempering is the second common way for heat treatment of X210Cr12 steel. This heat treatment is famous under the name “quenching for second hardness” and it is used for preparing of stamping dies which work up to 400 – 500 °C at high wear and friction conditions. The aim of this paper is to show some results from the metallographic study of the microstructure of X210Cr12 tool steel with and without modifying additions of nano-sized Si<sub>3</sub>N<sub>4</sub> after high temperature quenching and tempering.

Key words: metallography, high-chromium tool steel, heat treatment

**M-6**

**SURFACE MODIFICATION OF TOOLS BY EDM IN ELECTROLYTE**

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In this work a novel technique for surface modification of metals and its application for obtaining higher hardness and wear resistance of tools is described. The electrical discharge machining in electrolyte gives a modified surface with specific combination of properties in result of non-equilibrium microstructural characteristics. The surface layers have a different structure in comparison with the metal matrix and higher hardness, wear resistance and corrosion resistance. The modification goes by a high energy thermal process in a very small volume on the metallic surface involving melting, vaporization, activation and alloying in electrical discharges, and after that cooling of this surface with high rate in the electrolyte. The high energy process put together with the non-equilibrium phase transformations in the metallic system causes considerable modifications of the metallic surface and obtaining of layers with finecrystalline and nanocrystalline structure. The investigations show that obtained on tool steels layers have a very high hardness which give considerable increasing of working life of tools and wide opportunities for industrial application.

Key words: surface modification, tool steels, EDM in electrolyte

**M-7**

**EFFECTS OF STEELMAKING PROCESS AND HEAT TREATMENT  
PROCEDURES ON THE ULTRA HIGH STRENGTH STEEL PROPERTIES**

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An investigation of the effects of the steelmaking process on the tensile and fracture toughness properties of the ultra high strength steel (UHSS) is presented in this work. Three different steelmaking technologies were performed for production an UHSS - Maraging steel with 18% Ni. Air induction melting followed by electron beam (EB) remelting, vacuum induction melting followed by EB remelting and vacuum induction melting followed by electric slag remelting (ESR) were applied for steel production. Obtained steel ingots were forged to bars and were heat treated according the standard procedure for maraging steel as quenching followed with aging. The influence of steelmaking procedures on basic mechanical properties and fracture toughness (K<sub>Ic</sub>) as well as dynamic fracture toughness (K<sub>Id</sub>) is assessed. Steels produced by all three steel making procedures show a good combination of high tensile properties and fracture toughness. Vacuum induction melting followed by ESR showed better operational features than the other two steelmaking procedures.

Key words: UHSS, maraging steels, steel production, steel properties

**M-8**

**MICROSTRUCTURE OF ANODE BUTTS**

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The electrolysis process, where alumina is reduced by carbon to produce aluminum, is the largest user of carbon anodes. There are two basic anode designs, the pre-baked anodes and the single, self-baking Soederberg anodes. Pre-baked carbon anodes are made from a mixture of calcinated petroleum coke as filler and coal tar pitch as binder formed into blocks and baked at 1150 °C. These anodes must be replaced at regular intervals. The remaining parts of spent anodes from the aluminum production are called anode butts. To improve the economics of the process, the cleaned anode butts are crushed and reused in the production of new anodes. About 20% of the anode is recycled material.

This work deals with the results of investigation of the anode butts microstructure. Microstructure was determined using the method of optical microscopy. Microstructure have important role in the reactivity of a carbon anode. The active surfaces found primarily in micropores, are connected by higher CO<sub>2</sub> reactivity as well as inorganic contents to have higher air reactivity and wear of the anode.

Key words: aluminum, electrolysis, anode butts, microstructure

**M-9**

**INFLUENCE OF STRUCTURAL-TEXTURAL CHARACTERISTICS OF  
MINERAL ASSOCIATION ON CHALCOPYRITE LEACHING BY SODIUM  
NITRATE IN SULPHURIC ACID**

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During the chalcopryrite leaching by sodium nitrate and sulfuric acid solution, leaching rate decreases with increasing the time and a part of chalcopryrite mineral grains remain in the leach residue. Influence of structural-textural characteristics of mineral association on chalcopryrite leaching by sodium nitrate in sulfuric acid solution was studied in this paper.

In chalcopryrite concentrate, 92 % of sulfide minerals occur as in liberated grains, and the rest is in association with gangue minerals. Complex forms, like impregnations and complex intergrowths, almost do not exist. Chalcopryrite, the most abundant sulfide mineral (77%), occurs in liberated grains (96 %), which is very favorable from the aspect of hydrometallurgical treatment.

After experiments were carried out, leaching of copper achieved 84 % at temperature 80 °C and time of 240 min. In the all of the leach residues, over 97 % chalcopryrite mineral grains occur as liberated with highly corroded surfaces. Therefore, the structural assembly of chalcopryrite grains is favorable and there is no reason to reduce the leaching rate in the final stage of reaction.

The SEM/EDX analysis of the leach residues confirms the formation of elemental sulfur during the leaching. It also indicates that the sulfur, which was formed during the reaction, precipitated at the particle surfaces, and slowed down the leaching rate in the final stage of the leaching process.

Key words: chalcopryrite, leaching, sodium nitrate, sulfuric acid.

**M-10**

**LABORATORY OBTAINING OF FERROALLOY AFTER REDUCTION OF  
OXIDES FROM WASTE PRODUCT AND NATURAL RESOURCE**

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The Obrochishte deposit located in the Republic of Bulgaria has considerable reserves of relatively poor carbonate manganese ore. At the same time, in the country there are operative outputs for the production of sulphuric acid where vanadium catalyst is deactivated and discharged, polluting the environment. The utilization of these materials requires their consolidation to proper sizes with regard to the next processing, as the most suitable method for joint consolidation is agglomeration. The present work explores the preliminary calculations for obtaining agglomerate and obtaining an alloy with high and low carbon content, through carbothermic and aluminothermic agglomerate reduction.

Key words: manganese ore, vanadium catalyst, agglomeration, complex alloy.

**M-11**

**CHANGES OF MECHANICAL PROPERTIES OF HIGH STRENGTH LOW  
ALLOYED STEEL AFTER QUENCHING AND TEMPERING**

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The comprehensive investigation of tempering behavior of a HSLA (high strength low alloyed) steel, containing 0,30 % C; 0,90 Si; 0,92 % Mn; 1,00 Cr, was carried out. This steel attains its full characteristics after quenching and tempering. The influence of tempering parameters, such as: hardness, tensile characteristics and elongation, were determined.

The obtained results helped out the completion of the investigated steel database, thus enabling the choice of optimal tempering parameters, to suit the specific application in practice.

Key words: HSLA steel, tempering, mechanical properties

**Acknowledgement**

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**M-12**

**QUALITY IMPROVEMENT OF AS CAST Al ALLOYS WITH  
ELECTROMAGNETIC FIELD APPLICATION**

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The quality of as cast ingots is of great importance because it implies a greater efficiency of Al alloys production process. Presented results were obtained from microstructure examination of Al alloys 2024 and 7075 casted with and without electromagnetic field. The microstructure was examined after the metallographic preparation and etching in Keller's reagent and anode oxidation with Barker's reagent. For the quantitative microstructure analysis the image analysis device Leica Q500MC was used.

The microstructure characterization shows that a finer and more homogeneous microstructure was obtained through the entire cross section of ingots casted with electromagnetic field, compared to ingots casted without electromagnetic field. The results also reveals better surface quality of as cast ingots and possibility to eliminate energy and time consuming step, such as the surface machining.

Key words: Al alloys, electromagnetic field, microstructure

**M-13**

**MORPHOLOGY OF ELECTROPHORETICALLY DEPOSITED  
HYDROXYAPATITE COATINGS ON 316LVM STAINLESS STEEL**

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The electrophoretic deposition (EPD) is a rather old technique used here with a novel spray-dried nanostructured hydroxyapatite (HAp) powder in order to obtain uniform and dense hydroxyapatite coatings. This was done to overcome the restrictions of previously used high temperature coating techniques and to overcome the complex geometry metallic substrate problems. The EPD operating conditions, such as deposition voltage, current, concentration and time are parameters to control the coating thickness and morphology.

The coating of nanosized hydroxyapatite was electrophoretically deposited on grit blasted surface of stainless steel 316LVM samples at constant voltage, for different deposition times and was subsequently sintered in vacuum and argon atmosphere at 960 °C 1000 °C and 1040 °C.

The HAp powder thermal stability was initially assessed using DTA-TG analyses over the temperature range of 23 °C-1000 °C. The microstructure characterization of the coating was accomplished using SEM, and phase composition was determined by XRD.

The influence of the deposition parameters, such as time and temperature on the coating morphology was investigated in this work.

Keywords: EPD coatings, hydroxyapatite, 316LVM stainless steel

**M-14**

**POROSITY AND CRYSTALLINITY OF PLASMA-SPRAYED HAp  
COATINGS ON THE 316LVM STAINLESS STEEL**

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The porosity and crystallinity of atmospheric plasma-sprayed HAp coatings on the 316LVM stainless steel, ordinarily used as a standard material for hip implants production are presented in this paper. The commercially available HAp powder was deposited with different spray parameters, such as gasses Ar/H<sub>2</sub> and N<sub>2</sub>/H<sub>2</sub> combination, flow-rate (1.5- 5 g/s), spray power (25-75 kW) and stand-off distance (100 – 250 mm). Quality requirements for HAp coatings, besides phase composition, Ca/P ratio and microstructure, are porosity and crystallinity. There are opposed opinions concerning porosity and crystallinity, while it has been suggested that an ideal HAp coating for orthopedic implants would be the one with low porosity, and a high degree of crystallinity. The other documents, however, indicate that an amorphous coating may be more beneficial for better bone ingrowth than a coating with high crystallinity.

The obtained structure of plasma-sprayed HAp coatings varies from an amorphous phase at the interface to a crystalline outer surface. The lower crystallinity at interface is probably caused by a higher cooling rate of first layers deposited onto the substrate. The crystallinity was evaluated by the XRD analysis.

The porosity of the coating should also meet the optimum of the opposite requirements. It should be dense with low porosity to keep its consistency, and on the other side it should be porous enough to enable the bone ingrowth. The porosity of the coating was determined on the microstructure photographs using the software application Quick Photo Industrial 2.2.

The coatings microstructure characterization was accomplished using optical microscope Carl Zeiss Axovert CA 25, at magnifications of 200 x and 500 x.

Key words: HAp coatings, crystallinity, porosity, 316LVM stainless steel

**M-15**

**APPLICATION OF EXOTHERMIC FERROALLOYS FOR STEEL  
ALLOYAGE, DEOXIDATION AND DEGASIFICATION**

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This paper presents a detailed and precise description of the entire process of exothermic ferroalloy production, as well as techno-economic advantages of their steel alloyage application, compared to traditional ferroalloys that are in use today. The paper also points out to a material composition of exothermic ferroalloys, i.e. presents the properties of all composition components. That primarily refers to the components that ensure exothermic quality of ferroalloys, (Al-powder and swarf from the hot steel rolling mill), welding flux components for regulation of slag composition and its flowability, used as an admixture for the exothermic effect increase in the course of steel alloyage. In the framework of the detailed description, the devices for semi-industrial production are presented in the pictures. A brief economic assessment of justifiability of application of this technological solution is also presented, indicating that the costs of exothermic ferroalloy production are lower than ferroalloy application, which is a result of the reduction of scale and increase of thermic aggregate efficiency. The results of the practical application of the technology in alloyage process by exothermic ferrochrome, ferromanganese and ferroniobium briquettes are also presented. They indicate that the inclusion of alloying elements with the use of exothermic ferroalloys in form of briquettes is higher in comparison to traditional alloyage methods. The increased use of Mn accounted for 16 %, Cr for 13.5 %, and ferroniobium for 5-10 %, proving the justifiability of the application of exothermic ferroalloys produced by the mentioned technology.

Keywords: exothermic ferroalloys, ferrochrome, ferromanganese, ferroniobium

## M-16

# MASTERING THE TECHNOLOGY OF PREPARATION OF SLAG FROM THE OXYGEN PROCESS STEEL PRODUCTION FOR RECYCLING AND MANUFACTURING OF PRODUCTS FOR OTHER INDUSTRY SECTORS

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It is known that the slag formed in the course of the oxygen convertor steel production process drains into settling tanks of different dimension and supplied with a concrete outflow drain. In this tank, the slag is exposed to water for the purpose of self-grinding, in order to enable magnetic extraction of large metal pieces, which are conveyed to a steel factory for recycling. The non-magnetic segment, which accounts for 80% of the total molten slag, is removed and deposited at slag dumps, which, from one hand, present a serious ecological problem, and on the other hand, causes a problem that affects a regular course of primary steel production. This paper, therefore, presents a technological solution which transforms slag deposited at slag dumps into a material for a broad industrial application by means of a defined technology. This solution essentially involves its grinding and magnetic separation. Magnetic materials containing significant amount of iron of various granulation are used in iron and steel metallurgy as a substitute for iron ore and steel waste. Non-magnetic fractions, depending on their granulation, may be applied in sinter production as a welding flux substitution, in road construction industry for lower layers of road construction, in agriculture as a fertilizer, as a sandblasting material, as a road sprinkling material for winter conditions, etc. Finally, on the basis of mass balances, the economic effects are presented, clearly indicating that the above-mentioned technological solution practically eliminates the need for slag dumps, which resolves a serious ecological problem, but also substitutes, to a significant extent, natural resources necessary for primary steel production.

Keywords: slag convertor, magnetic separation, non-magnetic fractions, agriculture

**M-17**

**EFFECT OF ALLOYING ELEMENTS ON THE SEGREGATION AND  
DISSOLUTION OF  $\text{CuAl}_2$  PHASE IN Al-Si-Cu ALLOYS**

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The hypoeutectic aluminum alloy Al-6%Si-3.5%Cu was used in the present study to investigate the effect of diverse alloying elements on the dissolution of the copper phase ( $\text{CuAl}_2$ ) during solution heat treatment. Elements such as Sr and P were added to the base alloy individually and in various combinations. The cooling curves of these alloys were obtained by solidifying the alloy melts in a preheated graphite mold (600 °C, cooling rate  $\approx 0.6$  °C/s). The first derivative curves were plotted and used to determine the effect of the additives on the precipitation temperature of the Al-CuAl<sub>2</sub> eutectic reaction. Microstructural examination was carried out using optical microscopy, image analysis and electron probe microanalysis, with energy dispersive X-ray (EDX) analysis system. Samples from different alloys were dissolved under heating at 505 °C for various times up to 100 hours. The results explicitly reveal that solution heat treatment plays a critical role on the dissolution of the  $\text{CuAl}_2$  phase. It was found that Sr led to segregation of the  $\text{CuAl}_2$  phase away from the Al-Si eutectic regions, which slowed down its dissolution during solution heat treatment. However, phosphorus addition had a negative effect on  $\text{CuAl}_2$  dissolution due to its solubility in the  $\text{CuAl}_2$  phase particles, and the formation of oxide particles which act as nucleation sites for the precipitation of the block-like  $\text{CuAl}_2$  phase. It retards the complete dissolution of this copper phase even after 100 hr solution treatment.

Key words: Al-Si-Cu alloy, segregation, dissolution

**M-18**

**THE IMPACT OF THE METALLURGICAL CHANGES ON THE WELD  
JOINT QUALITY**

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High-frequency electric resistance welding (HFERW) is one of the most extensively used methods for production of longitudinal welded carbon steel pipes suitable for line pipe, casing and tubing. In this pipe production process, the hot rolled strip goes into the forming mill where it is gradually cold formed into a tubular shape in several stages of forming rolls and its edges are continuously joined by a combination of localized electrical resistance heating and forge pressure. HFERW generally involves high temperature, mechanical pressure and subsequent cooling, and as the result of this, thermal cycle causes significant metallurgical changes. These metallurgical changes have considerable impact on the high frequency electric resistance weld joint quality.

This paper deals with the analysis of the impact of the metallurgical changes on the weld joint quality of the longitudinal welded carbon steel pipes Ø114.3 x 5.21 mm.

Key words: metallurgical changes, weld joint, steel pipes.

**M-19**

**EFFECTS OF SPIN CASTING ON THE MICROSTRUCTUE AND  
MECHANICAL PROPERTIES OF ALUMINUM ALLOYS**

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The possibility of obtaining new microstructural features and varied mechanical properties using spin casting is the thrust of this work. Casting is a manufacturing process by which a liquid material is poured into a mold, which contains a hollow cavity of the desired shape, and then allowed to solidify. The solid casting is then avoided or broken out to complete the process. Casting may be used to form hot liquid metals or various materials that *cold set* after mixing of components (such as epoxies, concrete, plaster and clay). Casting is most often used for making complex shapes that would be otherwise difficult or uneconomical to make by other methods. Spin casting is a process of producing castings by causing molten to solidify in rotating moulds. The quality of the final spin casting mainly depends upon many parameters such as: pouring temperature, initial temperature of the mould, rotating speed and size of the mould, time of pouring into the mould, composition of the composite, type, diameter and shape of particles and others. Spin casting is widely used for production of parts, in which molten metal is poured at suitable temperature into rapidly spinning mould. Spin casting is suitable to produce parts which are free from internal shrinkage voids. In this research, investigation of microstructure and mechanical properties of spin cast aluminum alloy was carried out. A spin casting machine was designed and constructed and tested to spin cast aluminum alloy at different rotating speeds. As received aluminum scrap was subjected to spectrometric analysis to determine the chemical composition. The aluminum alloy scraps were melted to produce samples using spin casting and stationary moulding methods. The hardness properties and microstructural features of the new cast products were determined by subjecting each to hardness test using a universal digital hardness tester and microstructural assessment made using an optical microscope linked with an image analyzer to determine on comparative basis the properties exhibited by each samples as a basis of evaluating the new cast product to their as received samples. Spin casting technique and the control of other casting variables such as pouring temperature and pouring rate, speed of rotation were found to influence the microstructure and the hardness value of cast products. It was concluded that the different moulding and casting methods adopted brought about microstructural changes which affected the mechanical properties.

Key words: Moulding, Spin-casting, microstructure, mechanical properties

**M-20**

**FORMABILITY OF STEEL GRADE C10D2 BY COLD ROLLING**

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The influence of the conditions of plastic deformation by cold rolling on the microstructure and the formability of the steel grade C10D2 is the subject of this paper. The steel samples were cold rolled with different deformation degree up to 90% and after that the samples were annealed. The cold deformation was done by laboratory two-high rolling stand with plain rolls. After the rolling, the steel sheets were annealed.

The formability of the sheets in the cold rolling process and after the annealing was analyzed following their microstructural and mechanical changes. The qualitative and quantitative metallographic analysis of the obtained microstructure was done. The size of the ferrite grain was determined. Also, the influence of the conditions of the plastic deformation on the formability of the sheets was analyzed through their hardness changes.

The metallographic analysis has shown the significant influence of the deformation degree of the cold rolling process on the orientation and the banding into the rolling direction. The results of the annealing indicated that the recrystallization process is characterized with decreasing of the toughness and hardness properties as well as the increasing of the formability of the sheets of steel C10D2.

Key words: formability, cold rolling, steel, annealing, microstructure

**M-21**

**INFLUENCE OF DEFORMATION PARAMETERS OF HOT ROLLING ON  
THE EDGE WAVES OF THE MANGANESE STEEL PLATES**

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Surface flatness of the hot rolled steels is a crucial property requirement for any steel plant. The appearance of the edge waves in the hot rolling process of the manganese steel plates has been studied in this paper. The influence of the deformation parameters of the hot rolling process on the edge waves was analysed. Hot rolling was performed in industrial conditions, in Makstil A.D. Skopje.

The geometrical parameters of the sheets in the course of deformation were followed, as well as some of the more important parameters of the hot rolling process – reduction degree, temperature, velocity and rolling force in each pass. At the end the measurements of the flatness of the produced sheets were conducted in order to determine the edge waves.

The influence of the more significant parameters of the rolling process – velocity, temperature and rolling force, on the appearance of edge waves was followed. The obtained knowledge point out that quality sheets without edge waves are produced at higher rolling velocity, higher rolling temperatures and lower rolling forces.

Key words: hot rolling, edge waves, manganese steel plates

## M-22

### MECHANICAL PROPERTIES MODELLING OF IRON ORE SINTER

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The main functions of presented models are: a quick and reliable prognosis of its metallurgic properties, as well as defining conditions for production of optimum quality sinter, used for blast furnace production. The testing of these functions was carried out, at the level of experiment planning and experimentally.

The differences between the prognosticated values and the values obtained by the model, as well as between the values obtained experimentally, in semi-industrial conditions, proved the reliability of the model for practical application. The obtained models enable optimization from the aspect of those properties (reducibility, mechanical strength, and disintegration on reduction low temperatures) on which parameters of the blast furnace production (coke consumption, the uniform rate operation of blast furnace, etc.) depend on.

Mathematical correlation was determined between reducibility of ore and contents of limonite (L), hematite (H) and magnetite (M) according to following equation:

$$R = 0.727 - 0.004L + 0.04H + 0.003M$$

Mechanical strength of the sinter is:

$$M.C. = 54.740 + 0.05L + 0.075H - 0.034M$$

Presented equations show that reducibility increases with the increase of limonite and hematite and less with the increase of magnetite content. The content of magnetite in the ore mixture decreases the mechanical strength of sinter.

Keywords: sinter, mineral composition, reducibility, mathematical correlation, blast furnace

**M-23****DETERMINATION OF KINETIC PARAMETERS OF HETEROGENEOUS  
SULPHATIZATION ROASTING PROCESS OF MANGANESE  
CARBONATE WITH FERRO SULPHATE IN ISOTHERMAL CONDITIONS**

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Kinetics of heterogeneous sulphatization roasting process of composite  $\text{MnCO}_3/\text{FeSO}_4$  in oxidative atmosphere was examined. Experimental studies were focused on defining the kinetic parameters of manganese sulphatization process as a function of temperature. Kinetics of the process of sulphatization of manganese in isothermal conditions, is defined by application of a model exponential equation  $\alpha = \alpha^{\infty} (1 - \exp(-Kst^{0.5}))$ , which applies to the overall kinetic diffusion area of the chemical manganese sulphatization process. Manganese sulphatization process regime was investigated in the temperature interval from 723 to 1073 K. Obtained values of activation energy  $E_{a1} = 86.91$  kJ/mol for the specified temperature interval (723-873 K) and  $E_{a2} = 29.01$  kJ/mol for a temperature interval (873-1073 K) show that the process is carried out in two stages. First period is inductive period which represents thermal dissociation of the components in the system – chemically controlled process that occurs in the kinetic region. In the second period, substitution period, sulphatization of manganese takes place, where the process turns into diffusion controlled area.

By applying electronic raster microscopy, microscopic analysis of the sulphatization of manganese was conducted. Obtained results for pressed composite  $\text{MnCO}_3/\text{FeSO}_4$  in the temperature interval (723-1073 K) indicate the influence of temperature change to the shape change of the polyedra crystal grains into granulated grains. From the obtained energy spectra it can be concluded that increasing temperature results in transformation of manganese carbonate into the sulphated form.

Keywords: Sulphatization process kinetics, activation energy, composite  $\text{MnCO}_3/\text{FeSO}_4$

## M-24

# COMPARISON OF CHARACTERISTIC MICROSTRUCTURES BETWEEN SIMULATED SPECIMENS AND REAL WELDMENTS IN HAZ OF OPTIM 700 MC HIGH STRENGTH STEEL

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In this research work characteristic microstructures in the HAZ of TIG and laser bead-on plate weldments were determined and compared with simulated specimens. Thin sheets from Optim 700 MC high strength steel (TMCR) were used as base material.

One autogenous, automatic TIG, weldment was carried out. CO<sub>2</sub> bead-on-plate laser welding was performed too. As a shielding gas was used helium with a flow rate of 20 l/min.

Simulation of the influence of thermal cycles on microstructure of HAZ was performed on a Gleeble 1500 welding simulator. The following parameters were used for thermal simulation:

- Heating rate: 500 °C/s,
- Peak temperature: 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300 and 1350 °C,
- Holding time: 1 s,
- Cooling time,  $\Delta t_{8/5}$ : 1, 71 s (air cooling).

After bead-on-plate welding (TIG and laser) and Gleeble thermal simulation, hardness measurement and metallographic investigations were performed to simulated specimens and real weldments. Hardness in the welded joints was measured along the line, beneath the surface of the weldments at distance of 0.5 mm between measuring points. In all cases load of 2 kg was used. Nine measurements are made on every simulated specimen, and hardness is given as an average value. Standard procedure for metallographic preparation of specimens was performed. Chemical etching (Nital 5%) was used for determination of microstructure and grain size.

Metallographic analyze was performed to discover typical microstructures in the HAZ. As the most characteristic temperature points in the HAZ was discovered the following:

- 1350 °C – temperature of the coarsest austenitic grain size,
- 900 °C – temperature of the finest grain size,
- 800 °C – temperature of intercritical transformation start.

These characteristic microstructures were found in the real TIG and laser weldments. But, the width of completely HAZ was generally different as result of different heat input in both welding processes.

Keywords: welding simulator, HAZ, microstructure, laser welding, TIG welding

**M-25**

**STUDY OF THE INFLUENCE OF THE TYPE OF CARBURIZING ON THE QUALITY ON GRAY CAST IRON OBTAINED IN INDUCTION FURNACES**

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The aim of the research is to determine the impact of different types carburizing agent on the quality of gray cast iron, obtained in induction furnaces.

Applying methods for intensity melting at a dose and compound fines of metal components and carbon components will lead to obtain cast iron with the set up and properties with minimal use of blast - furnace cast iron. Along with that will provide a reliable method for processing cast iron shavings and other waste metals with large under 5 mm.

Still in practice have not found the optimal shape and size carburizing agent and sufficiently effective technology was inserted into liquid metal, which will be one of the main purposes of research.

Keywords: carburizing agent, gray cast iron, induction furnaces

**NANOMATERIALS (NM)**

## NM-1

# PREPARATION OF NANO-SCALED ANATASE BY THERMAL TREATMENT OF SOL-GEL PRODUCED $Ti(OH)_4$ AT DIFFERENT TEMPERATURES

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Titania, the naturally occurring oxide of titanium, is an inexpensive, innocuous, stable and environmentally friendly material with wide range of technical and technological applications such as: catalyst (chemical, photochemical and electrocatalysis), pigment, optical devices, sensor, sunblocking material in cosmetics, binder in medicine etc. Recently, the nanostructured materials with their unique physical properties (mechanical, optical, catalytic etc.) entirely different from those of the conventional micro- or millimeter sized materials, offer wider and more effective applications. In this context, all crystallographic forms of nano-sized  $TiO_2$  particles are of great importance and interest within the modern science and engineering application.

This study is concerned with development of sol-gel method for preparation of nano-scaled anatase form of  $TiO_2$  using organometallic precursor – titanium tetraisopropoxide and determination of the present crystalline phases depending on the temperature of further thermal treatment. The characteristic processes and transformations during the thermal treatment were determined by means of TGA/DTA method. The temperatures of the further thermal treatment were chosen according to the characteristic points determined by TGA/DTA analysis. In order to decompose  $Ti(OH)_4$  into  $TiO_2$  and to remove the residual amount of organic groups, the powder was heated for 2 hours in chamber furnace in the air atmosphere at different working temperatures (250, 380, 550, 650 and 800 °C). The working temperatures of the thermal treatments were 20–30 °C above the determined points.

The crystalline structure and size of the  $TiO_2$  crystallites were analyzed by means of Raman spectroscopy and XRD method. At 250 °C cryptocrystalline structure was detected, where amorphous  $TiO_2$  is accompanied with crystalline anatase. The anatase crystallite phase is stable up to 650 °C whereas at higher temperature rutile transformation begins. It was observed that at 800 °C almost the entire  $TiO_2$  is transformed to rutile phase. Morphology of the formed  $TiO_2$  aggregates was observed by scanning electron microscopy (SEM).

Key words: sol-gel synthesis, thermal treatment,  $TiO_2$ , anatase, crystallites size.

## NM-2

# PREPARATION OF NANO-SCALED RUTILE BY THERMAL TREATMENT OF SOL-GEL PRODUCED $\text{Ti}(\text{OH})_4$ AT OXIDATIVE AND REDUCTIVE ATMOSPHERE

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Titanium dioxide is chemically stable, non-combustible, non-toxic compound characterized by a high refractive index. These qualities make  $\text{TiO}_2$  widely applicable as a pigment for paint and varnish, plastics, paper, rubber, ceramics, pharmaceutical, food, and cosmetics industries. As result of its semi-conductive characteristics, it is used as catalyst for photochemical degradation of many organic pollutants in the air or water as well as for photoelectrochemical energy production. Nano-scaled titania is suitable for gas sensing applications. The stable form of titania is rutile, to which the other forms of titania transform at sufficiently high temperatures. Rutile is more suitable than the other forms (anatase and brookite) for application as a pigment and sensors for humidity.

The subject of this study is development of sol-gel method for preparation of nano-scaled  $\text{Ti}(\text{OH})_4$  using organometallic precursor – titanium tetraisopropoxide and its further thermal decomposition into rutile. The temperature of the thermal treatment at which rutile phase is stable was determined by means of TGA/DTA method. The thermal treatment was performed in oxidative (air) and reductive (10%  $\text{H}_2$  + 90%  $\text{N}_2$ ) atmosphere. The presence of lattice defects, possibly oxygen vacancies as result of reductive rutile transformation, is an important factor to form visible light sensitive photocatalysts. Also, it is known that non-stoichiometric titanium oxides show very high electrical conductivity that is suitable for electrocatalytic purposes.

Characterization of the produced nano-scaled rutile powders was performed by means of XRD, Raman spectroscopy, SEM, TEM and EDS analysis. In all samples rutile crystalline structure was detected. It was found that in oxidative atmosphere, rutile nanorods with diameter of near 10-20 nm were formed. In reductive atmosphere, granular particles were formed with diameter near 40 nm.

Key words: sol-gel synthesis, thermal treatment, reductive and oxidative atmosphere, rutile.

### NM-3

## NANO-SCALED HYPO-HYPER D-ELECTRODE MATERIALS BASED ON NON-NOBLE METALS AIMED FOR HYDROGEN EVOLUTION: EFFECT OF SUPPORT MATERIALS

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A very important issue within the hydrogen economy, as the most promising energy system in the future, is the choice of the electrode materials in hydrogen electrolyzers/fuel cells, on which hydrogen evolution/oxidation and oxygen evolution/reduction occur. The commercial application of the still leading electrode material – Pt is limited due to its high cost and low abundance. So, the main goal of the modern science employed is to reduce or even to replace platinum in the membrane electrode assembly (MEA), without losing the level of efficiency. There are two main approaches to achieve this: i) exploration of synergetic mixture of non-platinum electrocatalytic materials, e.g., according to Jakšić's hypo-hyper d-concept and ii) replacement of the traditional carbon support materials, e.g., Vulcan XC-72 with carbon nanotubes (CNTs).

This work is concerned with preparation and characterization of nano-structured composite electrocatalytic material for hydrogen evolution based on Co as a hyper d-metallic phase and anatase (TiO<sub>2</sub>) as a hypo d-phase, both deposited on different support materials. The following support materials were used: i) Vulcan XC-72, ii) Vulcan XC-72 with TiO<sub>2</sub>, iii) multi-walled carbon nanotubes (MWCNTs, as-prepared and activated) and iv) Magneli phases, *i.e.* nonstoichiometric titanium oxides. A comparison of catalytic activity of Co-based electrocatalysts deposited on all support materials mentioned is given.

Co-TiO<sub>2</sub> electrocatalyst deposited on activated MWCNTs exceeds the catalytic activity of the traditional Pt electrocatalyst deposited on Vulcan XC-72.

Key words: non-platinum electrocatalysts; support materials; anatase; hydrogen evolution.

## NM-4

### GOLD NANOPARTICLES AS A REDOX CATALYST

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The unique physical and chemical properties of gold nanoparticles such as chemical stability, specific optical and surface characteristics make them suitable modifiers of various surfaces used in the fields of optical devices and biosensors. The major goal of this work was to test the activity of gold nanoparticles as a redox catalyst. The study was carried out by means of cyclic voltammetry in combination with organic film-modified electrodes. The deposition of gold nanoparticles at the liquid interface formed between the organic film (o) and the aqueous phase (aq) was conducted via a spontaneous heterogeneous redox reaction between decamethylferrocene (DMFC)(o) and  $[\text{AuCl}_4]^{-}(\text{aq})$ . The deposition of gold nanoparticles has been conducted at an open circuit conditions (*ex situ* deposition) and by permanent cycling of the electrode potential in the course of the repetitive cyclic voltammetry (*in situ* deposition). It was demonstrated that the gold nanoparticles deposited on the liquid-liquid interface act as bipolar electrodes that catalyze the transfer of electrons between the DMFC(o) and different redox components present in the aqueous phase (e.g., vitamin C(aq),  $\text{H}_2\text{O}_2(\text{aq})$ ,  $[\text{Fe}(\text{CN})_6]^{4-}(\text{aq})$ , and three-peptide glutathione (GSH(aq))). The catalytic activity hardly depends on the deposition protocol.

Key words: gold nanoparticles, liquid interface, electrocatalysis

## NM-5

### SWELLING KINETICS OF POLYPROPYLENE NANOCOMPOSITES

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Sorption and diffusion of the solvents in and through polymers have been widely investigated from both theoretical as well as experimental point of view. The swelling technique is a commonly used method to determine various parameters, such as diffusion, sorption, and permeability coefficients. In swelling experiments, the polymer of known dimension is dispersed in a solvent, and the solvent mass uptake versus time is recorded and the data is used to calculate certain coefficients, important for the use of polymers in various applications such as membranes, ion-exchangers, controlled release systems, packaging, microchip manufacturing, etc.

In this study, neat isotactic polypropylene (iPP), modified m-iPP and m-iPP/organo-modified clay nanocomposites, prepared by melt intercalation, were studied for sorption kinetics in three solvents, having different solubility parameters: chloroform, carbon tetrachloride and dioxane. After melt extrusion, the samples for the analyses were produced by compression molding, and as a result of the cooling regime, materials with different morphology were obtained. Morphological analysis performed by wide-angle X-ray diffraction (WAXD), scanning and transmission electron microscopy (SEM and TEM) analysis indicates formation of exfoliated and/or mixed (intercalated/exfoliated) structure, depending on the amount of clay and the applied molding regime.

The objective of this work was to study the swelling kinetics of m-iPP nanocomposites containing orago-modified nanoclay, obtained under different conditions of compression molding, and as a result possessing different morphology and level of intercalation. It was shown that the presence of the silicate layers has decreased the solvent permeability due to reduced diffusion of solvent molecules that must bypass impenetrable platelets, the effect especially pronounced for the nanocomposites with dominant exfoliated structure. The obtained results are in agreement with our previous findings related to the morphology of the modified iPP nanocomposites with low clay content (up to 3 wt%).

Keywords: polypropylene, nanocomposites, swelling.

## NM-6

# EFFECT OF PROCESSING CONDITIONS ON THERMAL AND THERMO-MECHANICAL PROPERTIES OF POLYPROPYLENE NANOCOMPOSITES

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Polymer nanocomposites have been extensively studied during the last decades. The interest toward nanoscopic fillers in polymeric materials has originated from the fact that the composite materials exhibit enhanced material properties (e.g. mechanical, thermal, optical and gas-barrier properties) with relatively low filler content (1-5 wt %) compared to the pristine polymers.

The object of the study was to examine thermal and thermo-mechanical properties of polypropylene/organo-modified clay nanocomposites prepared by single-step extrusion process, using maleic anhydride grafted polypropylene (PP-g-MA) as a compatibilizer. After extrusion, the nanocomposite samples for the analyses were produced by pressing, applying cooling rates of 1 and 15 °C min<sup>-1</sup>, and as a result of the cooling regime, materials with different morphology were obtained, as revealed by wide-angle X-ray diffraction (WAXD). Predominant exfoliated structure of nanocomposite containing 1 wt% clay and mixed intercalated/exfoliated structure at higher nanoclay loading (3 wt% clay), as confirmed by WAXD and scanning/transmission electron microscopy (SEM/TEM), was achieved for nanocomposites produced at cooling rate of 1 °C min<sup>-1</sup>.

Thermal stability of matrix PP and nanocomposites in inert (N<sub>2</sub>) and air atmosphere were investigated by thermal gravimetric analysis (TGA). The influence of morphology on thermal stability of nanocomposites was analyzed by comparing oxidation induction time (OIT). The results revealed improved thermal stability of nanocomposites, obtained at slow cooling, represented by lower mass loss after isothermal treatment at 200 °C (the temperature of 50 % mass loss was shifted for 60 °C).

The thermal-mechanical stability of nanocomposites was investigated by dynamic-mechanical thermal analysis (DMTA). Nanocomposites obtained during melt slow cooling exhibited better mechanical properties as compared to neat PP and fast cooled samples (for 55 % at  $T > T_g$ ), respectively.

Key words: polypropylene, clay, nanocomposites, properties.

**NM-7**

**STUDY OF ELECTROLYTIC REDUCTION INTO LITHIUM AND SODIUM  
MOLTEN HYDROXIDES**

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Electrolytic reduction of both lithium and sodium molten salts on carbon and molybdenum cathodes accompanied with formation of graphene was studied by means of cyclic voltammetry. As an electrolyte LiOH and NaOH were used. The measurements were performed in temperature interval from 400 to 600°C. It was found that start potential of Li and Na reduction depends on type of electrolyte and cathodic material as well as working temperature. Due to intercalation of Li and Na into graphite bulk, electrochemical reduction on to graphite cathode occurs at more positive potentials related to molybdenum one. Increase of working temperature intensifies electron transfer on graphite electrode, shifting potential at more positive values. It should mention that the process of lithium and sodium intercalation generates a high mechanical stress at the graphite surface that causes exfoliation of the graphite cathode. This phenomenon enables electrochemical synthesis of grafen to be possible.

**Key words:** Graphene, Molten salts, Lithium, Sodium, Graphite

**ORGANIC CHEMISTRY (O)**

O-1

**INVESTIGATION OF QSRR PREDICTION OF RETENTION PARAMETER  
OF SELECTED S-TRIAZINE DERIVATIVES**Lidija R. Jevrić<sup>1</sup>, Sanja O. Podunavac-Kuzmanović<sup>2</sup>

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1,3,5-Triazines (s-triazines) are a class of compounds well known for a long time and are still being the object of considerable interest, mainly because of their applications in agriculture as the basis for various herbicides. Liquid chromatography is one of the most powerful analytical tools for organic compound analysis. The advantages of using chromatographic methods include: selectivity, chromatographic integrity and rapid method development. In view of the above-mentioned and in continuation of our studies on QSRR analyses, the goal of this investigation was to elucidate the quantitative effect of molecular structure of some s-triazine derivatives on their retention parameter.

In this context, a liquid chromatography method has been developed and validated for the determination of mathematical models for prediction of the lipophilicity s-triazine compounds. The correlation between retention factors,  $R_M^0$ , of several s-triazine derivatives and their physico-chemical and structural properties has been studied by TLC on RP-C18 silica gel.

The correlations between the retention constants,  $R_M^0$ , and selected lipophilicity parameter (different molecular descriptors) of the solutes were expressed by multiparametric equations of high statistical significance, indicate that these models can be used to predict the retention constants of these molecules.

The MLR statistics confirmed the importance of the hydrophobic interactions in the total retention mechanism of the investigated s-triazine compounds. Predictive ability of the MLR model and equations based on physically meaningful parameters allow us to estimate the lipophilicity of similar compounds.

**Key words:** s-triazine derivatives, retention parameter, molecular descriptors, quantitative structure-retention relationship.

O-2

## QSAR PREDICTION OF ANTIFUNGAL ACTIVITY OF SOME BENZOXAZOLE DERIVATIVES

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The benzoxazoles are a large class of organic compounds used as antimicrobial agents against a wide spectrum of microorganisms. The high therapeutic activity of the related drugs has encouraged the medicinal chemists to synthesize a large number of novel chemotherapeutic agents. The incorporation of the benzoxazole nucleus is an important synthetic strategy in drug discovery. This class of molecules have broadened the scope in remedying various dispositions in clinical medicine. This heterocyclic system has different activities as it can act as bacteriostat or bactericide, as well as fungicide, and it is present in numerous antiviral drugs.

In view of the above-mentioned and in continuation of our studies on QSAR analyses, the goal of this investigation was to elucidate the quantitative effect of molecular structure of some benzoxazole derivatives on their inhibitory activity against *Candida albicans*. The main objective was to establish a quantitative structure-activity relationships (QSAR) and derive a high-quality model which would link the structure of these compounds with their inhibitory activity.

The best QSAR model predicting the antifungal activity of the investigated series of benzoxazole was developed. The validity of the model has been established by the determination of suitable statistical parameters. The established model was used to predict inhibitory activity of the benzoxazoles investigated and close agreement between experimental and predicted values was obtained. The low residual activity and high cross-validated  $r^2$  values ( $r^2_{CV}$ ) observed indicated the predictive ability of the developed QSAR model. It indicates that the antifungal activity of series of benzoxazole derivatives can be successfully modeled using different molecular descriptors.

Key words: benzoxazole derivatives, antifungal activity, molecular descriptors, quantitative structure-activity relationship.

## O-3

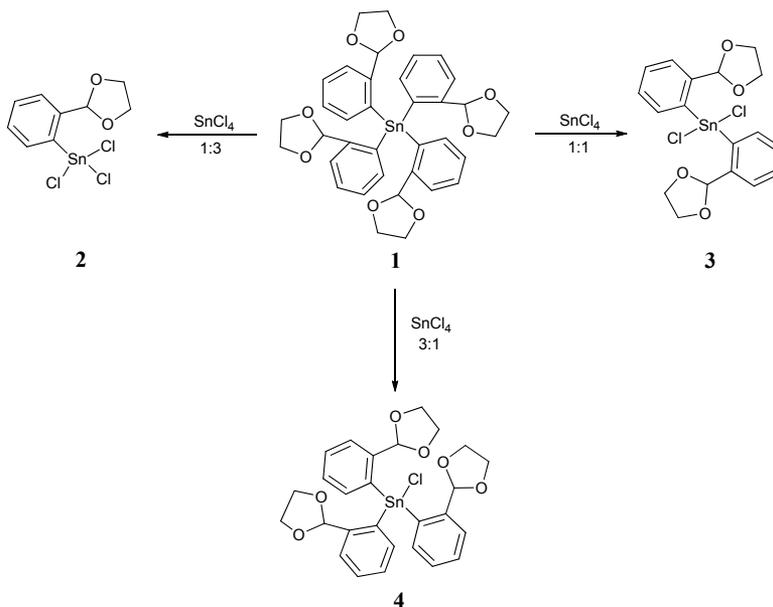
## SYNTHESIS AND CHARACTERIZATION OF NEW HYPERVALENT ORGANOTIN(IV) DERIVATIVES

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Organotin(IV) chlorides,  $[\{(CH_2O)_2CH\}C_6H_4]_2SnCl_3$  (**2**),  $[\{(CH_2O)_2CH\}C_6H_4]_2SnCl_2$  (**3**) and  $[\{(CH_2O)_2CH\}C_6H_4]_3SnCl$  (**4**), were obtained by reacting  $[\{(CH_2O)_2CH\}C_6H_4]_4Sn$  (**1**) with  $SnCl_4$  in 1:3, 1:1 and 3:1 molar ratio. Different reaction conditions were employed for optimal yield. The organotin(IV) compounds (**1-4**) were characterized in solution by NMR spectroscopy and their molecular structures in the solid state were established by single-crystal X-ray diffraction analyses. These compounds are useful starting materials for the synthesis of new organotin(IV) compounds and some reactions and products will be also presented.



Keywords : organotin, hypervalent

## O - 4

**CORRELATION OF CHROMATOGRAPHIC RETENTION DATA AND *IN SILICO* PROPERTIES OF SOME NEWLY SYNTHESIZED BENZIMIDAZOLE AND BENZTRIAZOLE DERIVATIVES**Vesna Dimova<sup>1</sup>, Natasa Milosevic<sup>2</sup>, Nada Perisic-Janjic<sup>3</sup>

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Benzimidazole drugs are used in both human and veterinary medicine, while benztriazole derivatives act as agonists for many proteins (proteases for example). The chromatographic behavior of newly synthesized benzimidazole and benztriazole derivatives has been studied by reversed-phase thin-layer chromatography.  $R_M^0$  values derived by extrapolation from reversed-phase chromatography were correlated with the lipophilicity  $\log P$  calculated by use of the commercial program ACD/logP. Good correlation was obtained. Retention constants  $R_M^0$  can be used to express the lipophilicity of the compounds investigated.

The relationships between chromatographic data and selected structural features of analytes that are believed to markedly affect their processes of absorption, distribution, metabolism, excretion and toxicity (ADMETox) were determined. Significant relationships were found between the retention constants,  $R_M^0$  and the *in silico* calculated molecular descriptors. In order to analyze the influence of lipophilicity on biological activity, lipophilic constants,  $R_M^0$ , were correlated with *in silico* calculated pharmacokinetic properties: human effective permeability in jejunum (Peff), corneal permeability (Pcornea), logarithm of the blood-brain barrier partition coefficient (logBBB), human plasma protein binding as percent unbound (UnbProt), human volume of distribution (Vd [l/kg]) and blood-to-plasma concentration ratio (RPB). Compounds of group A are predicted to have greater Peff and both groups of investigated compounds have demonstrated linear change of permeability when correlated with  $R_M^0$ . However, when RPB, Pcornea, logBBB and Vd values predicted for the investigated compounds were correlated with  $R_M^0$  two linear correlations with great statistical quality were obtained. Namely compounds were divided into two groups not by the core (benzimidazole and benztriazole), but according to substituent on position 2 or 4 attached to benzene: the first group - compounds with halogens and nitro group and the second group - compounds with methyl group or without substituent. Finally, between UnbProt and lipophilic constants  $R_M^0$ , parabolic relationship with good statistical quality was determined. For this novel series of compound the influence of the substituent on position 2 or 4 attached to the benzene core is expected to be predominant on lipophilic character and on its pharmacokinetic behavior (absorption through cornea, blood-brain membrane and to its distribution in the human body).

Keywords: benzimidazole, benztriazole, RPTLC, ADMETox, logP.

## O-5

**SELENOCYCLIZATION REACTION OF  
5-METHYL-5-(4-METHYL-PENT-3-ENYL)-IMIDAZOLIDINE-2,4-DIONE**

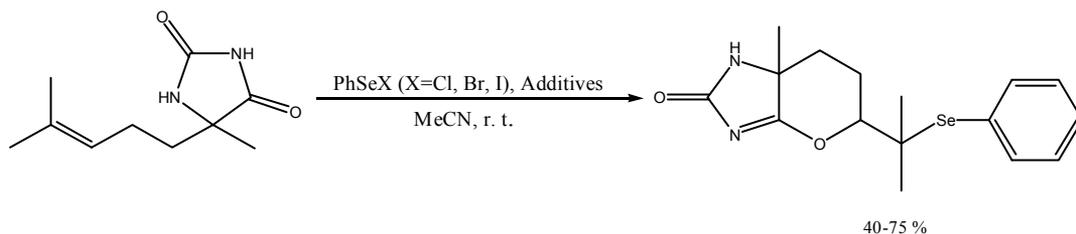
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The hydantoin moiety occurring in various biologically active compounds represents a pharmaceutical importance most notably known due to their antimicrobial activity.

The cyclization reaction of 5-methyl-5-(4-methyl-pent-3-enyl)-imidazolidine-2,4-dione with PhSeX (X = Cl, Br, I) in acetonitrile at ambient temperature was investigated. The nitrogen atom is incorporated in a functional group with other nucleophilic atoms which can give rise to competitive reactions leading to different heterocycles. The production of cyclic imidate derivative seems to be preferred contrary to lactamization. Also, the influence of the nature of counterion of selenilating agent as, well as the presence of some additives, like pyridine and some Lewis acids, on reactivity and regiochemical and stereochemical outcome of the cyclization was studied.



Keywords: hydantoins, cyclization, selenium reagents, Lewis acids

O-6

**DETERMINATION OF THE DISSOCIATION CONSTANTS OF SOME *p*-  
SUBSTITUTED AROMATIC HYDRAZONES**

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The hydrazones are a well-known class of organic compounds with a wide spectrum of biological activity which depends on the pH values of the media. Because of that, the behaviour of these compounds in acidic and basic media is very significant.

The changes in the UV spectra of five *N-p*-nitrobenzaldehyde-*p*-substituted benzoylhydrazones were followed in pH range and at ionic strength of 0.1 mol/dm<sup>3</sup> (NaClO<sub>4</sub>). The equilibrium between the ionic forms in the solution was investigated in ethanol-water (1:1) mixtures. The two absorption bands (198 nm and 330 nm) appeared in the spectrum of all investigated hydrazones in neutral medium. The hypsochromic shift of the second absorption band is observed in acid solutions, while this absorption band shifted bathochromic in basic solution. It suggests that the protonation (acidic medium) and dissociation (basic medium) reactions took place.

The possible site where the protonation take place, as well as, the site where the molecule loses proton is discussed using the values of the proton affinity and enthalpy of deprotonation calculated with AM1 and PM3 semi-empirical methods. The obtained results demonstrated that the protonation and dissociation process occurred in one step of hydrazone molecule. The exception is the hydrazone with phenol group on the benzene ring which causes two dissociation processes.

The obtained spectrophotometric data from the solutions with different pH values are used to calculate the dissociation constant values. In order to obtain more precise results, the calculations are made from the absorbance values at four selected wavelengths. Furthermore the  $pK_{BH}$  values are determined graphically from the intercept of the dependence of  $\log I$  on pH. The results showed that the numerically calculated  $pK_{BH}$  values are identical to those graphically obtained. The effect of the substituents on the protonation and dissociation behavior is also discussed.

Keywords: *p*-substituted aromatic hydrazones, protonation, dissociation, UV spectrophotometry, dissociation constants, semiempirical methods AM1 and PM3

O-7

**GLYCATION MECHANISMS STUDIED ON MODEL PEPTIDES**

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Glycation, also called non-enzymatic glycosylation, is a common modification in living organisms formed by the reaction of carbohydrates with free amino groups of peptides and proteins. The resulting early glycation products (Amadori compounds) can undergo further oxidative and non-oxidative degradation yielding advanced glycation end products (AGEs) – well-known markers of diabetes, Alzheimer's disease and ageing. Despite the high abundance of Amadori compounds in food and natural products, their relative impact in AGE accumulation is still unknown. Furthermore, AGE formation at the peptide/protein level is only partly characterized.

To fill this gap the model peptide Ac-AKASASFL-NH<sub>2</sub> was glycated with *D*-glucose for 0, 5, 15, 30 and 60 min at 95°C to simulate food cooking. The patterns of early and advanced peptide glycation products were characterized with reversed-phase high-performance liquid chromatography quadrupole time-of-flight mass spectrometry (RP-HPLC-QqTOF-MS) and the kinetics of their formation was determined. These results were matched to the degradation products formed during the incubation from glucose determined by gas chromatography-mass spectrometry (GC-MS) after derivatization with methoxyamine hydrochloride (MOA)/*N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA) and pentafluorobenzyl hydroxylamine. In order to determine the impact of Amadori compounds on the sugar and carbonyl products, degradation experiments with the same sequence glycated in the second position were performed.

Key words: Glycation, Amadori compounds, Glucose, Tandem mass spectrometry (MS/MS), Gas chromatography-mass spectrometry

## O-8

## MONO- AND DIBENZAMIDOMETHYLATION OF DIMEDONE. CARBON-CARBON FORMATION IN AQUEOUS MEDIA

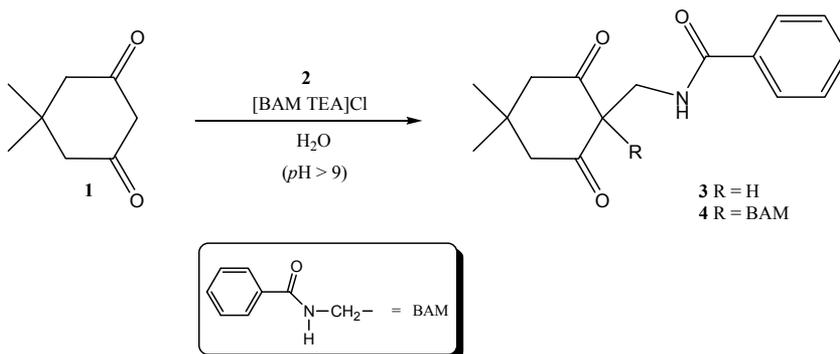
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In the present communication, the syntheses of the novel *C*-benzamidomethylated derivatives of dimedone are reported: 2-[(benzoylamino)methyl]-5,5-dimethylcyclohexane-1,3-dione and 2,2-bis[(benzoylamino)methyl]-5,5-dimethylcyclohexane-1,3-dione.

Carbon-carbon bond formation reactions between dimedone (**1**) and the (benzamidomehyl) triethylammonium chloride (**2**) were performed smoothly in aqueous media, under mild reaction condition and ambient temperature. The corresponding mono-*C*-benzamidomethyl (**3**) and di-*C*-benzamidomethyl (**4**) derivatives were obtained in excellent yields by controlling the stoichiometric ratio of the reactants. This method required neither organic solvent nor other catalyst.



The structures of the newly obtained compounds were confirmed by their  $^1\text{H}$  and  $^{13}\text{C}$ -NMR, UV-VIS and FT-IR spectra. Also, based on the UV spectra, the effect of reactions of mono- and di-*C*-alkylation on keto-enol tautomers was discussed.

Keywords: C-C bond formation,  $\beta$ -diketone, (benzamidomehyl)triethylammonium chloride

## O-9

## SYNTHESIS OF NOVEL *N*-BENZAMIDOMETHYL DERIVATES OF METHANESULFONAMIDE WITH POTENTIAL BIOLOGICAL ACTIVITIES

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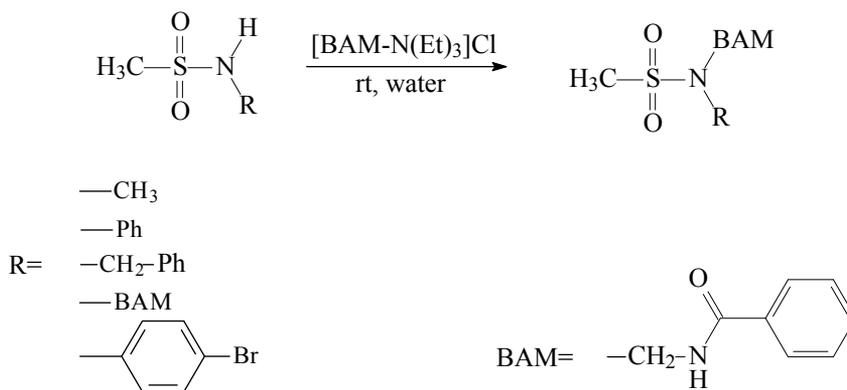
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In lieu to the growing threat of resistant strains of bacteria there is an urgent need for the development of new therapies for the treatment of bacterial infections. The sulfonamide drugs are well known for their antimicrobial activity. The sulfonamide moiety has also been reported in drugs that are not antimicrobials, such as diuretics, anticonvulsants, hypoglycemics, and HIV protease inhibitors. This is why there are a great number of research groups that work on the synthesis of novel, potentially biologically active compounds that contain the sulfonamide moiety.

Herein, we would like to report the synthesis of five novel *N*-benzamidomethyl derivatives of methanesulfonamide. The synthetic methodologies were straightforward, promoting mild conditions with mainly water as a solvent. The structures of the newly synthesized compounds were confirmed by means of NMR (<sup>1</sup>H, <sup>13</sup>C) as well as IR spectroscopy. In future perspective the antimicrobial activity of these compounds will be evaluated *in vitro*.



Key words: Sulfonamide; Antibiotic; *N*-benzamidomethylation

O-10

## A NOVEL BENZYLPIPERAZINE COMPOUND AS POTENTIAL SEROTONINERGIC AGENT

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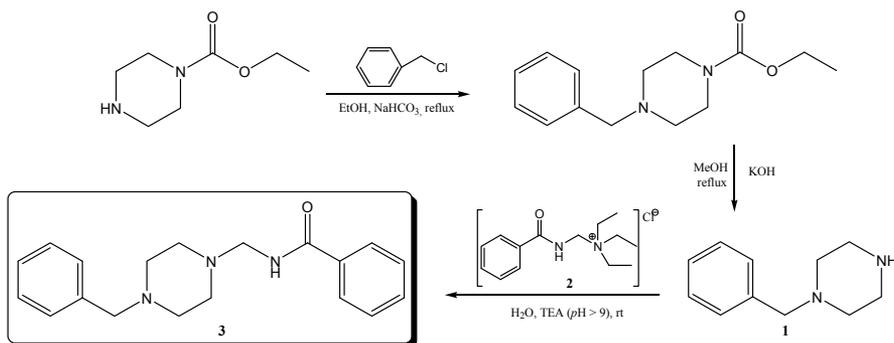
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Currently, much research effort is being focused on the discovery of highly selective serotoninergic agents. The reason for the interest in this area, derives from the possible involvement of 5-hydroxytryptamine (5-HT) receptors and 5-HT reuptake transporters in variety of neurological disorders including anxiety, social phobia, depression, migraine, premenstrual dysphoria and schizophrenia. 1-Benzylpiperazine (BzP) is the active agent in a number of designer drugs or “party pills” that are ingested for their psychotropic effects which may be indistinguishable from those of the amphetamines. The primary central neurochemical effects of BzP are like those that typify amphetamines, namely facilitation of the action of 5-HT through their non-exocytic release via interactions with 5-HT reuptake transporters. This action increases the concentration of serotonin in the synaptic cleft and thereby increasing activation of the surrounding serotonin receptors.

Herein we report the synthesis of a novel benzylpiperazine compound: *N*-[(4-benzylpiperazin-1-yl)methyl]benzamide.



The structure of the newly synthesized compound **3** was profoundly confirmed by NMR, FTIR spectroscopy and high-resolution mass spectrometry as well. For further reference of this compound, antidepressant and psychomotor stimulating activity *i.e.* behavioral effects of animal models after treatment with drug candidate will be evaluated.

Keywords: recreational stimulant, amphetamine-like effect, *N*-benzamidomethylation.

O-11

**CHARACTERIZATION OF THE POLYPHENOLIC CONTENT OF  
*Aronia melanocarpa* FROM MACEDONIA USING HPLC-DAD-ESI-MS<sup>n</sup>  
AND UV-SPECTROPHOTOMETRY**Elena Lazarevska, Jasmina Petreska and Marina Stefova

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Aronia fruits contain polyphenolic compounds that exhibit potential health benefits, such as antioxidant effects, inhibition of cancer cell proliferation, antimutagenic, cardioprotective, hepatoprotective, and antidiabetic effects. The polyphenol composition and antioxidant activity of samples of *Aronia melanocarpa* cultivated in Macedonia has been evaluated in this study using high-performance liquid chromatography (HPLC) coupled to UV-photodiode-array detection (DAD) and electrospray ionization mass spectrometric (ESI-MS) detection in the positive and negative ion mode, as well as Folin-Ciocalteu, pH-differential, and DPPH method. Extraction efficiency was studied in solvent mixtures containing methanol or acetone, water and acid, implying slightly better yield of polyphenols in acetone containing extraction solvents. DAD has been used for screening different classes of phenolic compounds, whereas MS and MS<sup>n</sup> fragmentation data were employed for their structural characterization revealing five groups of polyphenols: anthocyanins, flavonols, flavan-3-ols, hydroxycinnamic acid derivatives and conjugated forms of ellagic acid. Quercetin and kaempferol were the major flavonols found as aglycones and glycosides. Cyanidin derivatives were the most abundant anthocyanins in all samples.

Spectrophotometric measurements of total polyphenols, monomeric anthocyanins and radical scavenging activity has been employed as a more practical approach for fast quantification of these compounds in order to evaluate and compare the polyphenol content and antioxidant activity with published data. Total polyphenols determined by Folin-Ciocalteu were found in concentrations ranging between 12.3 g/kg and 13.8 g/kg expressed as gallic acid. The content of total monomeric anthocyanins obtained with the pH-differential method ranged between 4.5 g/kg and 5.3 g/kg expressed as cyanidin glucoside. Antioxidant activity varied from 74 to 86 μmol trolox equivalents/g.

The high content of polyphenols in aronia cultivars growing in Macedonia proves these berry fruits as rich source of health promoting compounds, which can be used as a raw material or additive in production of functional foods, such as fruit juice, spread, syrup, tea, etc.

Keywords: aronia, polyphenols, HPLC, mass spectrometry

O-12

**CHEMICAL COMPOSITION AND *IN VITRO* ANTIBACTERIAL ACTIVITY  
OF ESSENTIAL OILS FROM FLOWER BUDS OF  
*EUGENIA CARYOPHYLLATA***

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Plants and their components have been used as food complements and medicine since the ancient times. Today, they are mostly used in the cosmetic, pharmaceutical and the food industry, as well as in medicine. Most of the researches today are pointed towards finding natural plant components which will have an antimicrobial action without having contraindications in human organism. Cloves, the dried aromatic flower buds of *Eugenia caryophyllata*, are widely used and known for their antimicrobial components. That is the reason why clove essential oil (*Caryophylli floris aetheroleum*) can be used as a protection against pathogen microorganism, by inhibiting their cellular growth as well as killing them.

The antimicrobial action of clove essential oils was tested against several bacterial cultures. For this purpose, freshly isolated (hydrodistilled and dried) essential oil, commercial essential oil were used and compared to pure eugenol, the most active and most important component. The microorganisms used in the research are Gram positive (*Bacillus pumilus* NCTC 8241, *Bacillus subtilis* ATCC 6633, *Staphylococcus aureus* ATCC 6538 and *Sarcina lutea* ATCC 0341) and Gram negative (*Escherichia coli* ATCC 8739, *Pseudomonas aeruginosa* ATCC 9027 and *Agrobacterium rhizogenes* A4) bacteria. The microdilution test enabled determination of the minimal inhibitory concentration of all of three samples used in the experiment against all of test microorganism. It was concluded that the commercial and freshly isolated essential oil, as well as eugenol, have antibacterial characteristics and affect the growth of the gram positive and the gram negative bacteria. It was also found that the eugenol had the strongest effect against bacterial cultures, with the exception of *E. coli*, where the freshly isolated essential oil had the strongest bactericide effect. The commercial essential oil had the weakest action against all of test microorganisms. The chemical composition of all three samples was determined via GC-MS and preliminary connection between the methods of preparation and storage of essential oils and their antimicrobial properties was established.

Keywords: clove, essential oil, eugenol, microdilution method, minimal inhibitory concentration.

## O-13

## CHEMICAL COMPOSITION OF ESSENTIAL OIL ISOLATED FROM THE UNDERGROUND PARTS OF *VALERIANA OFFICINALIS* L.

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*Valeriana officinalis* L. preparations has been used for treatment of hysterical states, insomnia, migraine and rheumatic pains, and the essential oil isolated from roots can be used as a flavour in ice cream, baked goods and condiments. The *Valeriana radix* (Valerian) is very frequently used as a milder (herbal) alternative or substitute for synthetic sedatives in the treatment of insomnia. So far, the exact mechanism of Valerian action has not been established yet. It is believed that valerenic acid and the related sesquiterpenoid derivatives are responsible for the exhibited activity. The aim of this study was to optimize a GC-MS method for determination of the chemical composition of the essential oil isolated from the underground parts of *Valeriana officinalis* L. The special emphasis was placed on the presence and identity of the sesquiterpenoid derivatives. The roots of Valeriana samples yielded 3.1 ml/kg essential oil from the cut drug via hydrodistillation. The volatile constituents from roots of *Valeriana officinalis* L. were investigated using optimized GC/MS method. The GC/MS analysis was carried out on VF-5MS capillary column (30 m x 0.25 mm, film thickness 0.25 µm) with helium as a mobile phase with 1:50 split ratio and 1 ml/min flow rate. The following temperature program was used: 40 °C (3 min), then to 250 °C at 10 °C/min. In terms of the chemical composition, the main constituents of the essential oil were monoterpenes and sesquiterpenes and also, ester derivatives (acetates and isovalerates) were present in significant amounts. The basic oil components were isovaleric acid,  $\alpha$ -pinene,  $\alpha$ -fenchene, camphene, bornyl acetate, myrtenyl isovalerate, spathulenol, sesquiterpene alcohol, valerianol, valeranone and valeranal. The identity of the products was determined from mass spectra in electron impact (EI) mode by careful analysis of the fragmentation patterns and additionally by matching the mass spectra to library spectra (NIST 2005).

Valeranone (EI-MS)

Key words: *Valeriana officinalis* L., essential oil, monoterpenes, sesquiterpenes, GC/MS.

**O-14****NEW CONVENIENT VAPOR PRESSURE-TEMPERATURE CORRELATION FOR SOME ALIPHATIC HYDROCARBONS**Jane B. Bogdanov<sup>1</sup>, Bogdan T. Bogdanov<sup>1</sup>

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New empirical equations for correlating temperature dependence of vapor pressure for C<sub>6</sub>-C<sub>20</sub> aliphatic hydrocarbons are proposed:

$$\text{Log}_{10}(VP) = \frac{k_1 * T}{k_2 + T}$$

where, *VP* – vapor pressure, *T* – temperature, *k*<sub>1</sub> – asymptotic maximum vapor pressure, and *k*<sub>2</sub> – temperature at which the vapor pressure has half of its maximum value.

Descriptors *k*<sub>1</sub>, *k*<sub>2</sub> and *k*<sub>1</sub>/*k*<sub>2</sub> have physical meaning and are unique for a given liquid. This “uniqueness” can be exploited for quantitative description of vapor pressure-temperature curve. The equation given above can be transformed algebraically into other convenient forms for plotting experimental data such as:

$$\frac{T}{\text{Log}_{10}(VP)} = \text{Intercept} + \text{Slope} * T$$

$$k_1 = \frac{1}{\text{Slope}}; k_2 = \frac{\text{Intercept}}{\text{Slope}}$$

These derived descriptors can be utilized for evaluation and comparison of properties of different liquids and liquid mixtures and can serve as additional parameter for analysis of liquid hydrocarbon-based fuels for internal combustion engines

**Keywords:** Vapor pressure, vapor pressure- temperature equations, aliphatic hydrocarbons.

## O-15

**COMPARATIVE STUDIES OF AROMATIC ELECTROPHILIC NITRATION OF SUBSTITUTED BENZENES: REACTIVITY AND REGIOSELECTIVITY OF “MIXED ACID” REAGENT VERSUS SILICA GEL/HNO<sub>3</sub> REAGENT**Aljajdin Imerov<sup>1</sup>, Jane B. Bogdanov<sup>1</sup>

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Electrophilic aromatic nitration is one of the most widely used and important reactions in organic synthesis. Industrially the nitration of arenes is carried out by the mixed acid reagent *i.e.* mixture of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. The drawback of this procedure is that large excess of sulfuric acid is required, which afterwards requires cumbersome and costly removal and neutralization. The heterogeneous liquid/solid methods using supported reagents and/or catalysts are quite appealing due to the ease of handling, simple work-up and the potential to be recycled.

The aim of our work was to carry out a comparative study of the “classical” aromatic electrophilic nitration employing the mixed acid reagent (HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>) and the nitric acid supported on silica gel reagent (HNO<sub>3</sub>/SiO<sub>2</sub>). The main focus of our work was to determine the reactivity of the reagents, their selectivity and the yields. For this study the HNO<sub>3</sub>/SiO<sub>2</sub> reagent was prepared by treating the appropriate amount of silica gel with 7.5 M HNO<sub>3</sub> followed by filtration and air-drying of the nitrated silica gel. The nitric acid content of the silica gel was determined by titrating of water suspension with standardized 0.1 M NaOH. From our studies the acid content of the reagent was in the range of 16-20% by weight. After the appropriate reaction conditions and work-up the product ratios were determined by GC and/or GC-MS analysis. The identity of the products was determined from the comparison of retention times with authentic standard, by careful analysis of the fragmentation patterns of EI mass spectra and additionally by matching the mass spectra to library spectra (NIST 2005). In cases where unambiguous identifications were necessary the products were synthesized and purified using literature methods. The phenols and arylmethyl ethers were rapidly mononitrated by the HNO<sub>3</sub>/SiO<sub>2</sub> reagent at room temperature and in high yields. On the other hand, phenols and arylmethyl ethers were rapidly polynitrated with the HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> reagent. For deactivated substrates (Ar-X, X = NO<sub>2</sub>, CN, acyl) the HNO<sub>3</sub>/SiO<sub>2</sub> reagent is not suitable.

The HNO<sub>3</sub>/SiO<sub>2</sub> reagent proved to be quite promising for activated arenes, it is quite stable and suitable for handling and its activity can be potentially enhanced by addition of other catalyst.

**Key words:** electrophilic aromatic nitration, substituted benzenes, mixed acid reagent, HNO<sub>3</sub> /SiO<sub>2</sub> reagent

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## O-16

## CARBONYL-AMINE CONDENSATION OF 1,5-DISUBSTITUTED-INDOL-2,3-DIONE WITH CARBOHYDRAZIDE AND THIOCARBOHYDRAZIDE

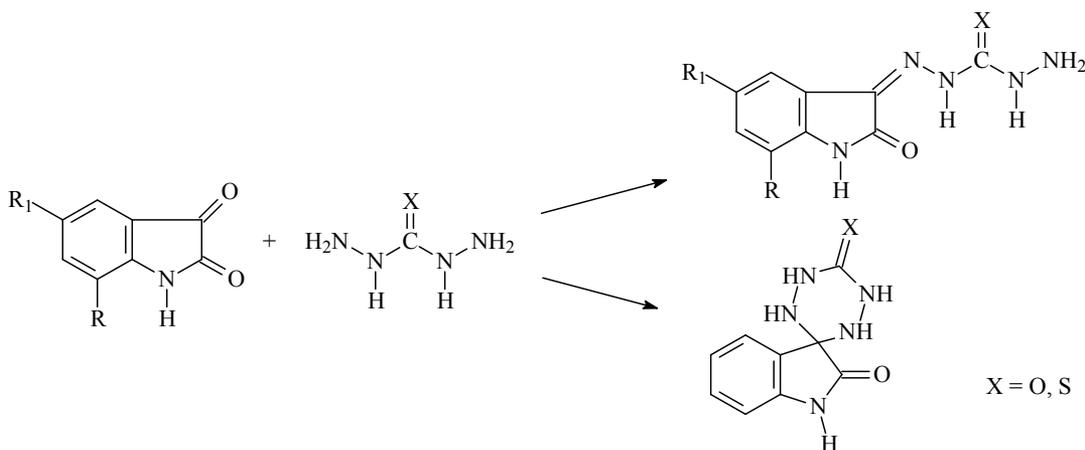
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The carbonyl-amine condensation of 1,5-disubstituted-indol-2,3-dione with carbohydrazide and thiocarbohydrazide was investigated. Mono carbohydrazons *i.e.* thiocarbohydrazons were obtained. The mono carbohydrazon was obtained by hydrazinolysis of diethylcarbonat. Its thio-analog, thiocarbohydrazide, was obtained with a slow thermolysis of hydrazine dithiocarbamic acid which was obtained by hydrazinolysis of CS<sub>2</sub>.

The reaction of carbonyl-amine condensation was carried out in neutral (water), weak acidic (ethanol) and acidic medium (acetic acid) by different ratios of the reactants. The mono (thio)hydrazons isolated appeared as a mixture of geometrical isomers. Among them the *syn*-isomer prevailed. The existence of another type of isomers (cyclic-acyclic isomers) with the monothiocarbohydrazons was established. During the reaction of 1-acetyl-5-Iodoindole-2,3-dione with thiocarbohydrazide in acidic medium, a new heterocyclic compound 2-oxo-1', 2', 4', 5'-tetrahydrospiro[3*H*-indol-3,3'-1,2,4,5-tetrazine]-6-thione was obtained.



Based upon their <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and IR spectra, the molecular structures of the synthesized thiocarbohydrazones were determined.

Key words: carbonyl-amine condensation, indole-2,3-diones, carbohydrazide, thiocarbohydrazide.

## O-17

**SYNTHESIS AND PESTICIDAL EXAMINATION OF  
CYCLOPENTANESPIRO-5-(2,4-DITHIOHYDANTOIN)**

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Different reaction pathways for synthesis of cyclopentanespiro-5-(2,4-dithiohydantoin) (**cpsdth**) are presented. Standard *in vitro* filter paper discs test with *Cladius pectinicornis* were conducted in order to be investigated eventual insecticidal activity of **cpsdth** against this pest on oil yielding roses (*Rosa damascena Mill*). Standard phytotoxicity vigor tests according to the EPA Ecological Effects Test Guidelines: OPPTS 850.4150 Vegetative Vigor, Tier I were conducted with oil-yielding rose plants (*Rosa damascena Mill*) flowering growth stage with tested product. The received data from conducted *in vitro* insecticidal test with *Cladius pectinicornis* were statistically manipulated with R language for statistical computing and drc R language package in order to be calculated values of LC05 (NOEL), LC50 and LC90. The results show the extremely high effectiveness of tested compound which was able to induce insecticidal effect on the tested pest at 0.011 % concentration as LC90 (0.0031 % as LC50), which is completely comparative with the insecticidal effect produced by active substances of most commonly used commercial insecticides on the market. This give grounds, the product (**cpsdth**) to be developed in the future as promising plant protection product with insecticidal activity.

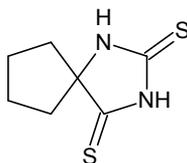


Fig. 1. Cyclopentanespiro-5-(2,4-dithiohydantoin)

Keywords: cyclopentanespiro-5-(2,4-dithiohydantoin), insecticidal activity, *Cladius pectinicornis*, *Rosa damascene*

Acknowledgements: Financial support by the Agricultural University – Plovdiv, Bulgaria (Contract 06-12) is gratefully acknowledged.

O-18

## STRUCTURE OF 2-(4-HYDROXYPHENYL)-SUBSTITUTED PHENALENE-1,3-DIONE AND INDAN-1,3-DIONE

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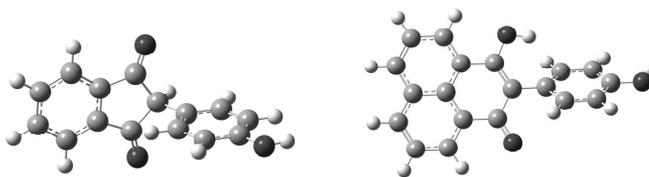
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The structure of 2-(4-hydroxyphenyl)-substituted indan-1,3-dione and phenalene-1,3-dione is investigated using a combination of solid-state NMR, single crystal X-ray analyses and quantum-chemical calculations. The synthesis of 2-(4-hydroxyphenyl)-phenalene-1,3-dione is described.



Keywords: 2-(4-hydroxyphenyl)-phenalene-1,3-dione, 2-(4-hydroxyphenyl)-indan-1,3-dione, solid-state NMR, X-ray, quantum-chemical calculations

Acknowledgements: We acknowledge the financial support by the Bulgarian Ministry for Education and Science under the Project BG051PO001/3.3-05-0001 „Science and Business”.



**POLYMERS AND POLYMER MATERIALS (P)**

P-1

## HYBRID COPOLYMERS WITH POLYPEPTIDE BLOCKS

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Polymer biomaterials with defined composition and properties are of particular importance in science due to their diverse applications as implants, in pharmaceutical formulations, controlled drug release, tissue engineering, etc. Synthetic block copolymers are the basis of a wide-ranging class of biomaterials. They are capable of self-association into aggregates with different morphology (micellar, cylindrical or complex structures), depending on the ratio between the block lengths, the solvent, the polymer concentration, the presence of additives, the change of temperature, the pH of the medium, etc. The self-association of block copolymers lies at the heart of the design of new materials and structures combining different properties. A major approach to the design of novel biomaterials is the formation of the so-called hybrid copolymers containing synthetic and polypeptide segments.

Hybrid copolymers built of polypeptide and synthetic polymers combine the functionality and biocompatibility of peptides and a range of structural and controlled properties of synthetic polymer segments. Accurate molecular design makes it possible to control the polypeptide structure and intermolecular forces, which, in turn, determines their applications.

In the present work, self-associating hybrid copolymers containing thermosensitive and polypeptide blocks were synthesized via controlled ring-opening polymerization of *N*-carboxyanhydride (NCA) of *Z*-*L*-lysine (*Z*-*L*-Lys-NCA), initiated by functional macroinitiators poly(*N*-isopropylacrylamide) containing 10 mol % of polyoxyethylene grafts and a terminal primary amine group (PNIPAm-*g*-PEO)-NH<sub>2</sub>.

The formation of the copolymers was confirmed using IR and <sup>1</sup>H NMR spectroscopy. Suitable conditions for the formation of complexes between the copolymers and DNA (polyplexes) were established. The sizes and surface charges of the polyplexes were determined by DLS and ζ-potential measurements. The cytotoxicity of the obtained hybrid copolymers and their complexes with DNA was evaluated with *HepG2* cell culture to establish their potential as gene delivery vehicles. It was found that there is no apparent cytotoxic effect of both hybrid copolymers and polyplexes (cell viability above 80% of controls).

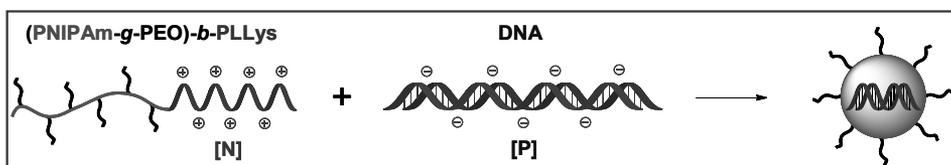


Figure 1. Formation of polyplexes.

Keywords: hybrid copolymers, (PNIPAm-*g*-PEO)-b-Plys, structure, polyplexes.

## P-2

**COMPLEXES OF HYBRID COPOLYMERS WITH HEAVY METALS AS CATALYSTS FOR OXIDATION**Emilya Ivanova<sup>1,2</sup>, Sevdalina Turmanova<sup>1</sup>, Krassimir Vassilev<sup>1</sup>, Ivaylo Dimitrov<sup>2</sup>

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Hybrid copolymers (HC) built of polypeptides and synthetic polymers are attractive materials because of the accurately controlled sequence of their constituent aminoacids and monomers. They combine the functionality of peptides with the diversity of structures and controlled properties resulting from the synthetic polymer segments. The presence of polypeptide blocks makes it possible to form interesting supramolecular nano-structures *via* hierarchical self-association in mass and in solution, largely due to the formation of structures typical of proteins by means of intra- and intermolecular forces. Accurate molecular design makes it possible to control the polypeptide structure and intermolecular forces. The low toxicity, high stability and proclivity for complex formation explain the use of hybrid copolymers in tissue engineering, as drug carriers, implants, etc.

The aim of the present work is to prepare metal complexes of hybrid copolymers having polypeptide blocks: (poly(*N*-isopropylacrylamide)-*g*-polyoxyethylene)-*b*-poly L-lysine -(PNIPAm-*g*-PEO)-*b*-PLLys and to study their catalytic activity in the reaction of oxidation of cyclohexene with *tert*-butylhydroperoxide.

Metal complexes of hybrid copolymers were prepared by complex formation in aqueous and organic solutions of salts of  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ . The optimal conditions for the formation of complexes between the hybrid copolymers and heavy metal ions were established. The studies carried out by FT-IR spectroscopy, UV spectroscopy and electron paramagnetic resonance proved the formation of metal complexes and one of their possible applications as catalysts for the oxidation of cyclohexene with organic hydroperoxides was shown. The activities of the complexes obtained towards cyclohexene epoxidation can be arranged in the following order:  $\text{HC-MoO}_2^{2+} > \text{HC-VO}^{2+}$ . It was found out that only cyclohexene oxide is selectively obtained in this reaction. The contents of cyclohexene oxide and 2-cyclohexene-1-ol reached 38.5 and 1.4 %, respectively. In the future, new approaches should be sought for the preparation of polymer carriers with suitable amphiphilic properties. Comparative experiments were carried out with complexes of the amino acids lysine and methionine.

Keywords: hybrid copolymers, (PNIPAm-*g*-PEO)-*b*-Plys, metal complexes, oxidation

**P-3**

**THERMAL STABILITY AND AGEING PROPERTIES OF SULPHUR CURED  
ETHYLENE PROPYLENE DIENE TERPOLYMER (EPDM) AND  
CHLOROSULPHONATED POLYETHYLENE RUBBER (CSM) AND  
THEIR BLENDS**

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The thermal stability of ethylene propylene diene terpolymer (EPDM) and chlorosulphonated polyethylene rubber (CSM) and their blends was studied by thermogravimetric methods. Aging characteristics of these rubber blends were studied by applying hot air oven thermal aging for seven days at 70 °C. The mechanical properties of the aged samples were studied. Thermal degradation and aging properties of these individual rubber and their blends were investigated with special reference to blend ratio. As the CSM content in the blends increased their thermal stability was also found to increase. DTG curves were used for the determination of different stages involved in the degradation. Activation energy for degradation was determined from Kissinger method. The properties of aged samples were found to decrease due to chain depletion. However, the mechanical properties (hardness, modulus and tensile strength) of CSM and EPDM/CSM blends were found to increase due to the formation of cross-links upon aging.

Key words : Rubber blends; Activation energy; Thermal stability; Ageing characteristics

P-4

**DISSOLUTION PROFILES ALLICIN AND PRODUCTS OF ITS  
TRANSFORMATION FROM MICROSPHERES BASED ON POLY  
(D, L-LACTIDE)**

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Polymers based on lactic acid deserve great attention due to their ability for decomposition in the human body into nontoxic metabolites. Biodegradable microspheres prepared from poly(D,L-lactide) have been widely studied in recent years and have become well established controlled drug delivery systems. Allicin (allyl thiosulfinate) has a wide spectrum of antibacterial, antiviral, and antifungal effect. Degradation products of allicin in no polar solvent, ajoene ((*E,Z*)-4,5,9-trithiododeca-1,6,11-trien-9-oxide) and vinylidithiins (2-vinyl-4*H*-1,3-dithiin and 3-vinyl-4*H*-1,2-dithiin) are also pharmacological active substances.

Poly(D,L-lactide) was obtained by microwave synthesis. Allicin was synthesized by acid oxidation of allyldisulfide, and transformed by using microwave in chloroform solution, at solvent boiling temperature, for 15 minutes. LC/MS chromatography was used for the qualitative and quantitative analysis of allicin and its transformation process. Microspheres were loaded with allicin and its transformants products (ajoene and vinylidithiine). The morphology of the microspheres was analyzed using a scanning electron microscope (SEM). Average size of microsphere was 50µm. HPLC method was used for assessment of allicine and allicine transformants releasing from microspheres at room temperature in solutions with different pH (pH=3 and pH=8) for 24 hours. Releasing of ajoene and vinylidithiine from the microsphere were much effective in acid solution. The process of release of active ingredients takes place in two phases. At the beginning there is leaching of active components from the surface of polymer microspheres, and afterwards there is continuous release process of diffusion from inside the microspheres.

Keywords: Poly(D,L-lactide), Microspheres, Allicin, Microwave polymerization

**P-5**

**REINFORCEMENT OF THERMOPLASTIC STARCH BY VARIOUS KINDS  
OF BENTONITE AND MONTMORILLONITE**

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Thermoplastic starch is a promising and well studied biodegradable polymeric material of natural provenience. It has potential to replace conventional oil-based non-biodegradable polymers especially in packaging industry. However, often low tensile strength of thermoplastic starch materials requires their reinforcement. It can be performed advantageously using clay or clay minerals, because these materials are able to form nanocomposites with polymer matrix. One particular type of montmorillonite (Cloisite Na®) is usually used in experiments involving starch/clay nanocomposites. This paper deals with thermoplastic starch reinforcement by bentonites as industrial minerals in comparison with conventionally used purified montmorillonite (MMT) clay. Mechanical testing results proved that natural bentonites contribute by similar level of reinforcement to thermoplastic starch matrix as the purified MMT.

Key words: thermoplastic starch, clay nanocomposite, montmorillonite, bentonite

P-6

## THERMAL BEHAVIOR OF MODIFIED UREA-FORMALDEHYDE RESIN WITH TiO<sub>2</sub> AND THIOSEMICARBAZIDE

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Polymer-based nano-composites consist of thermoset, thermoplastic or elastomeric matrices reinforced with nano-particles or nano-fibres. These materials are of great interest from an industrial and scientific perspective because they show much better behavior and characteristics in comparison with conventional composites. Thermal behavior of the organic-inorganic nano-composites prepared by a two-stage polymerization of urea-formaldehyde resin (UF) with thiosemicarbazide (TSC) and TiO<sub>2</sub> are investigated, and the impact of  $\gamma$ -irradiation on thermal stability of these nano-composites is studied. The two resins of urea-formaldehyde-TiO<sub>2</sub> nano-composites, namely; **Resin 1** (UF+TiO<sub>2</sub>) and **Resin 2** (UF + TSC + TiO<sub>2</sub>), are synthesized. The thermal behavior of obtained materials was studied by non-isothermal thermo-gravimetric analysis (TG), differential thermal gravimetry (DTG) and differential thermal analysis (DTA) supported by data from Fourier Transform Infrared Spectroscopy (FTIR). TiO<sub>2</sub>-based UF hybrid composites have been irradiated (50 kGy) and after that their radiation stability was evaluated on the basis of thermal behavior. The free formaldehyde percentage in all prepared samples was determined. DTG peaks of unmodified TiO<sub>2</sub>-based UF resin (UF + TiO<sub>2</sub>) are slightly shifted to higher temperature after  $\gamma$ -irradiation. For the case of **Resin 2**, DTG peaks have almost the same value before and after  $\gamma$ -irradiation. On this basis, we can conclude that the addition of TSC in the UF resin containing TiO<sub>2</sub> increased radiation stability. The minimum free formaldehyde percentage values (4%) for samples based on UF with TiO<sub>2</sub> and UF + TiO<sub>2</sub> + TSC after irradiation dose of 50 kGy are detected.

Keywords: Thermal behavior, urea-formaldehyde resin, radiation stability, free formaldehyde,  $\gamma$ -irradiation.

P-7

## ALL-CELLULOSE COMPOSITES BASED ON COTTON WOVEN AND KNITTED TEXTILE PRE-FORMS

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All-Cellulose composites were obtained based on the original concept of self-reinforced composite primary developed for thermoplastic high density polyethylene. These all-cellulose composites show substantial environmental advantages such as they are composed of sustainable resources, there is less interface between the fiber and the matrix, it possesses excellent mechanical and thermal performance during use, and they are fully biodegradable.

In this work “self-reinforced cellulose” or “all-cellulose” composites have been successfully prepared from two cotton textile preforms, wovens and knits, by means of a fibre surface dissolution method in lithium chloride dissolved in *N,N*-dimethylacetamide (LiCl/DMAc). Two different parameters have been studied: (i) surface treatment medium (alkaline/enzyme/bleaching) and (ii) cotton textile preforms (knits, woven). All-cellulose composites with 85–95% fibre volume fraction were successfully prepared by using solutions of 3 (wt/v) cellulose concentrations in 8 % (wt/v) LiCl/DMAc for impregnation of cotton textile preforms. The thermal, mechanical and structural properties of the all-cellulose cotton based composites were characterized using DSC, TGA/DTA, tensile tests and FTIR spectroscopy. The composite morphology was studied by scanning electron microscopy.

It was found that a dissolution time of 24 h lead to biobased materials with the best overall mechanical performance, as this time allowed for the dissolution of a sufficient amount of fibre surface to obtain good interfacial bonding between fibres, while keeping a considerable amount of remaining fibre cores that provide a strong reinforcement to the composite. Alkali treated Cotton knits have shown higher lateral crystalline index in the obtained composites compared to enzyme treated ones, although the composites based on enzyme and bleach treated pre-forms have shown the best mechanical properties.

Keywords: All-cellulose composites, Cotton, knits, wovens,

**P-8**

## **DETERMINATION OF EXTENSION SET IN ALBANIAN LEATHER**

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Leather is a natural material used in car upholstery and home arredation. When hides are converted to leather all non essential parts of the original animal hide are removed, leaving only the surface "grain" and middle "corium" layers. It is the remarkable structure of this corium made up of millions of microscopic fiber, twisted and interwoven by nature, that gives leather its highly tensile strength and other desirable qualities. This study is focused on determination of extension set in different albanian leather intended to use in upholstery but it is also aplicable to all flexible leather. A test piece is repeatedly extended at a specified rate until the forces reach a predetermined level and the permanent extension is calculated as a percentage of the original length. We used tensile testing machine having the appropriate force range  $20.0 \text{ N} \pm 0.5 \text{ N}$ . Selection of tests samples is done in a random way. Sampling is done in accordance with ISO Standards. The test pieces are cut into direction paralel to the backbone and perpendicular to the backbone. We have determined the mean percentage extension set, Es, in each direction.

Key words: leather, ISO standarts, extension set, parallel direction, perpendicular direction

**P-9**

**RAMAN, XPS AND UV CHARACTERIZATION OF IR LASER IRRADIATED  
POLY(PHENYLENE ETHER-SULFONE)**

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IR laser irradiation of poly(1,4-phenylene ether-sulfone) (PES) results in the formation of gaseous products: sulfur dioxide, carbon monoxide and unsaturated hydrocarbons. They reveal that the polar units of the polymer backbone are cleaved into simple CO and SO<sub>2</sub> molecules and that the phenylene unit is cleaved into smaller fragments. Deposited solid carbonaceous films were analyzed by Raman, XPS and UV spectroscopy. These spectra indicate that the deposited films possess sulfide and sulfoxide units and have a greatly diminished content of the initial sulfone groups. The laser process differs from the conventional pyrolysis of PES, which yields SO<sub>2</sub> and phenol as major volatile products and a carbonaceous char. More severe irradiation conditions favour extrusion of sulfur dioxide, whereas the milder ones make carbon monoxide and hydrocarbons formation more feasible.

Key words: poly(1,4-phenylene ether-sulfone); laser ablation; deposition of polymer films

**P-10**

**SEM AND EPR CHARACTERIZATION OF IR LASER IRRADIATED  
POLY(PHENYLENE ETHER-SULFONE)**

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TEA CO<sub>2</sub> laser-induced ablative decomposition of poly(1,4-phenylene ether-sulfone) (PES) yields in the formation of volatile products (SO<sub>2</sub>, CO, ethyne, benzene, CS<sub>2</sub>) and allows deposition of carbonaceous films possessing less SO<sub>2</sub> and CO bridges and sulfidic and sulfoxide groups. Morphology of the deposited films were characterised with electronic microscopy. The EDX-derived stoichiometry of these films reveals a significant decrease of the S and O elements as compared to the virgin polymer and shown that this decrease is more pronounced at the high fluence radiation. The deposited films obtained at high and low fluence were paramagnetic and their EPR spectra were sensitive function of the presence of oxygen, which suggested their use as a sensor for O<sub>2</sub>.

Keywords: poly(1,4-phenylene ether-sulfone); pulsed infrared laser-ablative degradation; deposited solid paramagnetic carbonaceous films.

**P-11**

**POLY(LACTIC ACID) /KENAF FIBER COMPOSITES: EFFECT OF MICRO-FIBRILLATED CELLULOSE ON INTERFACE-SENSITIVE PROPERTIES**

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Ecologically friendly composites consist of a biodegradable matrix and natural fibers (such as cotton, sisal, kenaf, bamboo, etc.), which have been successfully used for reinforcing of different polymer matrices. Quite recently, poly(lactic acid) (PLA) was used as a matrix for biodegradable eco-composites.

Natural fibers (NFs) offer both cost savings and a reduction in density when compared to glass fibers. Though the strength of NFs is not as great as glass, the specific properties are comparable.

One of the most undesirable properties of NFs is their dimensional instability due to the swelling caused by moisture absorption. However, a strong fiber/matrix interfacial adhesion can help to diminish the water penetration, avoiding the worsening of mechanical performances of composites exposed to humid conditions.

According to the literature, kenaf fibers exhibit higher strength values in terms of tensile and flexural properties, as compared to other NFs, when reinforcing PLA.

The aim of this work was to study the mechanical behavior of PLLA-based composites reinforced with kenaf fibers, and the influence of micro-fibrillated cellulose (MFC) on overall composite properties.

Composites of PLLA and kenaf fibers were prepared by melt mixing the components in a Rheocord apparatus, and consequent compression molding at 180 °C for 3 min at 50 MPa. The amount of MFC in the mixture was varied from 5-15 %, while the content of PLLA was kept constant, 50%.

The results have shown that the addition of MFC influence the interface sensitive properties of PLLA/kenaf fiber composites, increasing the interfacial energy release rate for about 20% at MFC loading of 10%. Flexural strength and modulus of the composites were also improved by the presence of MFC, reaching values of 57 MPa and 5.9 GPa, correspondingly.

Key words: kenaf fiber composites; biodegradable matrix; natural fibers; micro-fibrillated cellulose; interface-sensitive properties.

P-12

## THERMAL BEHAVIOR OF VULCANIZED RUBBER FILLED WITH CARBON BLACK

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Natural rubber (NR) and rubber composites are used extensively in many different applications and products, ranging from household to industrial products, including tires, tubes and bridge bearings.

Rubber compounds are often consisted of many components that are either reinforcing or non-reinforcing, including carbon black, calcium carbonate, clay, silica etc. The function of the reinforcing components is to improve rubber properties, basically mechanical and thermal, but also vulcanization and process properties, as well as to prolong lifetime of the product. The non-reinforcing fillers are generally used to increase bulk and reduce the cost of the rubber. The type and amount of the additives and cure agents/accelerators in NR depend on the final properties of the product.

The aim of the present work is to analyze the influence of several additives and curing accelerators on vulcanization process and thermal properties of NR SMR CV60 (Plasticity Retention Index - 60 min; Mooney viscosity - 60±5). For this purpose nine ingredients were gradually added to natural rubber matrix, and analyzed the thermal behavior of the mixture successively.

Differential scanning calorimetry experiments were carried out with a PE DSC-7 calorimeter in inert atmosphere, at heating/cooling rate of 10 Kmin<sup>-1</sup>. Thermogravimetric analysis was carried out with PE Dyanod TGA/DTG Analyzer with a heating rate of 10 Kmin<sup>-1</sup> in temperature range between 30 and 700 °C.

The obtained results were a good base for understanding the influence of the added additives on the thermal behavior and stability of NR and its content optimization as well.

**Keywords:** Vulcanized rubber, thermal stability, thermal behavior



**PROCESS ENGINEERING (PE)**

## PE-1

### PEPTAS: SOFTWARE DESIGNED FOR BATCH PINCH TECHNOLOGY

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Methodology of heat process integration depends on the type of processes that are present in certain facilities. According to that, Pinch technology is divided to methods for continuous and batch processes. Batch Pinch analysis is time dependent as batch processes. The aim of this work is to simplify the usage of the Pinch analysis for batch processes. The main task is the design of appropriate software. Procedure for this software is previously determined as procedure for heat streams analysis and heat exchanger network design. The software needs to analyze energy streams by using Pinch technology (TSM and heat storage) as well as analysis of profitability of designed solutions. Economic analysis is performed through Cash flow analysis and determination of economic parameters according to which, decision for the best solution will be made.

PEPTAS or Process Engineering – Pinch Technology Applied Solution is software, designed on the basis of algorithms for time analysis of selected streams, Gantt diagrams design, Pinch analysis of time dependant energy stream's combinations, as well as algorithms for economic analysis of developed solutions. The analysis of selected energy streams and algorithms are used to analyze the possibility of storing heat that is available in the system and is currently not possible to use in the direct heat exchange. The results obtained with the analysis made by PEPTAS, are compared with the analysis made by Pinch technology software for analysis of streams in continuous processes, adapted to the case of batch processes. Comparisons of the results show that there is no difference in results.

Keywords: software, Pinch technology, batch processes

**PE-2**

**THE STATISTICAL OPTIMIZATION OF THE HETEROGENEOUSLY-CATALYZED CONTINUOUS METHANOLYSIS**

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The researchers have put a lot of effort into developing an efficient process for biodiesel production. They often face the challenge of finding the effective catalyst, raw materials and optimal production conditions that will produce a biodiesel of required properties in an acceptable yield. Optimization of the production conditions is very important for maximizing the biodiesel yield and minimizing the production cost. When performed in a traditional way, a great number of experiments are needed to determine the optimal process variables, which is time-consuming. The efficient procedure for planning experiments, analysis of obtained data to get valid and objective conclusions is the statistical design.

In this work, the statistical analysis of the continuous heterogeneously catalyzed sunflower oil methanolysis was studied. The quicklime-catalyzed continuous process was conducted in a packed bed reactor with co-currently up-flow of the reactants through the reactor. The aim of the work was to study the influence of the methanol-to-oil molar ratio and the residence time on the fatty acid methyl esters (FAME) yield. In order to evaluate the significance of individual factors and their interaction effect on FAME yield, a  $3^2$  factorial design of experiments with replication and the analysis of variance were applied. The process was performed at 60°C under the atmospheric pressure. The methanolysis of sunflower oil was carried out at methanol-to-oil molar ratios of 6:1, 12:1 and 18:1 and residence times of 1.0, 1.5 and 2 hours. Both factors and their interaction were effective on the FAME yield at the 95% confidence level. The initial methanol-to-oil molar ratio had the largest effect, which resulted in greater FAME yields.

Keywords: ANOVA, biodiesel, methanolysis

### PE-3

## NUMERICAL EXPERIMENTS FOR STUDYING THE APPLICABILITY OF NONLINEAR FREQUENCY RESPONSE METHOD FOR INVESTIGATION OF GAS ADSORPTION

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Theoretical considerations have shown a great potential of the nonlinear frequency response method (NFR) method in dealing with gas adsorption equilibrium and kinetics. Knowing the second order FRF, besides the first order FRF, provides very accurate discrimination between different kinetic mechanisms and determination of the kinetic parameters of thorough nonlinear model. Estimation of the equilibrium and kinetic parameters from the same experimental data is an additional advantage of the NFR method. In this work an analysis of the applicability of the NFR method has been performed based on numerical experiments.

In order to produce “quasi-experimental” data, the pressure response of a batch adsorber is simulated for a sine waveform change of the volume around several steady-state concentrations, for different input amplitudes and over a wide range of frequencies. Obtained “quasi-experimental” responses were transferred into a frequency domain by fast Fourier transform and used for calculation of the first and second order FRF on the adsorber scale and corresponding FRFs on the particle scale. The coefficients of an adsorption isotherm were determined from the low-frequency asymptotes of the first and second order FRF on the particle scale. Mass transfer coefficient was obtained from the maximum of the imaginary part of the first order FRF on the particle scale. Obtained coefficients show good correlation with those used for simulations.

Additionally, some aspects that might influence the accuracy of the NFR method applied to the experimental data, as noise and number of analyzed data points, are considered. Second order FRF is found to be especially sensitive to the noise and number of analyzed data points.

Keywords: Nonlinear frequency response; Gas adsorption; Numerical experiments; Parameter estimation

## PE-4

### MODELING THE KINETICS OF RESINOIDS EXTRACTION FROM THE AERIAL PARTS OF WHITE LADY'S BEDSTRAW (*GALIUM MOLLUGO* L.)

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In this paper, the kinetic of resinoid extraction from the aerial parts of white lady's bedstraw (*Gallium mollugo* L.) using an aqueous ethanol solution (50% by volume) was studied at 23°C, 50°C and about 80°C and at 23°C, 30°C and 40°C in the absence and the presence of ultrasound (40 kHz), respectively. The main goal was to model the kinetics of the extraction process using three physical models: 1) the pseudo first order kinetics, 2) the model based on instantaneous washing followed by diffusion and 3) the model of simultaneous washing and diffusion. The parameters of models were determined by the multiple nonlinear regression using experimental values of the resinoid yield measured during the extraction. For the kinetic models 1, 2 and 3, the coefficient of determination ( $R^2$ ) was 0.462, 0.842 and 0.993, respectively, while the mean relative percent deviation (MRPD) was  $\pm 6.8\%$ ,  $\pm 4.0\%$  and  $\pm 2.9\%$ , respectively. The values of  $R^2$  and MRPD showed that the model that involved two simultaneous processes, washing and diffusion, could be recommended as the most successful for modeling the kinetics of resinoid extraction at different temperatures in the absence and the presence of ultrasound. It was also shown that ultrasound had an effect only on the washing process, but did not affect the diffusion through plant particles.

Keywords: *Galium mollugo*, Maceration, Ultrasound-assisted extraction, Kinetics.

**PE-5**

**THE USE OF ARTIFICIAL NEURAL NETWORK FOR PREDICTIION OF  
THE RESINOIDS EXTRACTION YIELD FROM *HYPERICUM  
PERFORATUM L.***

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The present work deals with the use of an artificial neural network (ANN) for predicting the yield of resinoids from a plant material (*Hypericum perforatum L.*) at different operating conditions of the extraction process. The main goal was to evaluate the work of ANN model for predicting the resinoid yield. The development of the ANN model consisted of the training, validation and testing processes. The ANN with the 5-10-1 topology was found to have the highest values of the coefficient of determination (0.998, 0.994 and 0.957) and the lowest values for mean square error (0.24, 0.31 and 5.85) for training, testing and validation processes, respectively. It was also shown an excellent correlation between the predicted and experimental values of the resinoids yield (the mean relative percent deviation values was only  $\pm 2.9\%$ ). The results indicated the ANN model could be successfully applied for estimation of the resinoid yields from *Hypericum perforatum L.*

Keywords: Extraction, Resinoid, *Hypericum perforatum*, Artificial neural network

**PE-6**

**FINITE-TIME STABILITY OF UNCERTAIN SINGULAR TIME DELAY SYSTEMS**

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Often Lyapunov asymptotic stability is not enough for practical applications, because there are some cases where large values of the state are not acceptable, for instance in the presence of saturations. In this case, the stability problem is solved by introducing the concept of finite-time stability. However, finite-time stability is less investigated for singular uncertain time-delay systems. In this paper, finite-time stability problem for a class of linear uncertain time-delay systems is studied. Firstly, the concept of finite-time stability is extended to linear uncertain time-delay systems. Then, based on matrix inequalities and the Lyapunov-Krasovskii like functions method, some sufficient conditions under which the linear uncertain time-delay systems are regular, impulsive-free and finite-time stable are given. The condition is translated to a feasibility problem involving linear matrix inequalities (LMIs). Finally, an example is employed to verify the efficiency of the proposed methods.

Keywords: singular systems, time-delay, finite-time stability, Lyapunov method

## PE-7

**KINETICS OF IN SITU EPOXIDATION OF CASTOR OIL CATALYSED BY  
ION EXCHANGE RESIN**

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Vegetable oils are valuable renewable resources for the chemical industry due to ability of their main constituents, triglycerides, to undergo various reactions. Epoxidation of double bonds in fatty acid chains of triglycerides is industrially exploited since epoxidized vegetable oils have wide application both as final products and intermediates. For example, after transformation of epoxy groups into hydroxyl groups, derivatized vegetable oils are used for obtaining polyurethanes. Castor oil is a natural polyol which has about 90% of hydroxy fatty acid, ricinoleic acid (12-hydroxy-9-octadecenoic acid), in its fatty acid composition. Therefore, it can be used for obtaining polyurethanes without previous derivatization. However, due to a presence of unsaturation in castor oil, formation of epoxy rings, which can be further transformed, is favorable. Although many reports concerning epoxidation of different vegetable oils can be found, very few deal with epoxidation of castor oil. Conventional method for epoxidation of vegetable oils with percarboxylic acid formed *in situ* from hydrogen peroxide and carboxylic acid, usually acetic or formic, in the presence of an ion exchange resin as catalyst has been applied to castor oil. Regarding kinetics, only the model for castor oil epoxidation with peracetic and performic acid formed *in situ* in the presence of the ion exchange resin, assuming pseudo-first order kinetics, has been proposed.

The objective of this work was to investigate the kinetics of the epoxidation of castor oil in benzene with peracetic acid generated *in situ* from acetic acid and hydrogen peroxide in the presence of an acidic cation exchange resin as the catalyst. A pseudo-homogeneous kinetic model was developed and, based on the experimental data for epoxidations run under different reaction conditions, model parameters were determined. Temperature dependency of the kinetic parameters was expressed by reparameterized Arrhenius equation. The constants of the Arrhenius equation were determined by fitting experimental data using the Marquardt method. The increase of all rate coefficients for considered reactions with temperature and positive values of the calculated reactant and product concentrations, indicate the correctness of the proposed pseudo-homogeneous kinetic model.

Keywords: Castor oil; *In situ* epoxidation; Peracetic acid; Ion exchange resin; Kinetic model

## PE-8

**PARTITIONING OF ACETIC ACID IN EPOXIDIZED SOYBEAN OIL-  
SOYBEAN OIL-ACETIC ACID-HYDROGEN PEROXIDE-WATER SYSTEM**

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Epoxidized soybean oil is widely used as final product, as well as intermediar in chemical industry. It may be produced by epoxidation of soybean oil with peracetic acid formed *in situ* from acetic acid (A) and hydrogen peroxide in the presence of an acidic catalyst. A valid mathematical model of this reaction system, necessary for design and optimization of the reactor, should include various kinetic, thermodynamic and mass transfer parameters since the reaction system is either two- or three-phase depending of a catalyst: former if mineral acid is used as the catalyst, and later if an ion exchange resin is used. In two-phase kinetic models partitioning of acetic acid between the oil and water phases should be taken into consideration by including a partition coefficient of A,  $K_{CA}$ , in the model.  $K_{CA}$  should be presented as function of liquid-liquid equilibrium constant of A,  $K_A$ , and molar volumes of the phases. For this system it is difficult to experimentally determine and to predict  $K_{CA}$ , therefore, better approach is to determine and correlate  $K_A$ .

The objective of this work was to experimentally determine dependency of the liquid-liquid equilibrium constant for acetic acid in a system epoxidized soybean oil-soybean oil-acetic acid-hydrogen peroxide-water from temperature and composition. The experiments were conducted by equilibrating the components of investigated system at different temperatures employing different compositions. The temperature, as well as a ratio of components in the mixture, was varied in the range that is usually applied in industry for epoxidation of vegetable oils. The ratio of components was also selected as to simulate change of components' concentrations that occurs during epoxidation.

Determined value of  $K_A$  ranged from 1.97 to 4.72. The results of this work will be further used to correlate and predict the partition coefficient of acetic acid.

Keywords: *In situ* epoxidation, Soybean oil, Acetic acid, Liquid-liquid equilibrium constant

Acknowledgment: This work is part of the Project #III 45022 supported by the Ministry of Education and Science of the R. Serbia.

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**PE-9**

**INFLUENCE OF COSOLVENT ON DISPERSED PHASE  
DROP SIZE IN A RECIPROCATING PLATE REACTOR**

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In this paper the drop size of the dispersed phase in the system consisted of sunflower oil, tetrahydrofuran (THF) and the solution of KOH in methanol was studied in a cocurrent upflow reciprocating plate reactor (RPR). The main goal was to estimate the influence of the THF concentration on the drop size distribution and the Sauter-mean drop diameter. The experimental setup consisted of a glass column (2.54 cm i.d.) and a set of 63 equally spaced perforated plates attached to the central shaft moving up-and-down. The amplitude and frequency of the reciprocating movement were 1.0 cm and 2 Hz, respectively. The reaction temperature and the oil:methanol molar ratio were 20 °C and 1:6, respectively. The THF concentrations were 1 and 10 % wt. The size of the drops was estimated from photographs taken along the column. For each set of operational conditions about 500-1000 drops were measured using a software package. The drop size distribution was found to be unimodal independently of operating conditions applied. The Sauter-mean drop diameter decreased with increasing the THF concentration and along the reactor column. Independently of the THF concentration, the mean drop size was smaller in the reactive than in the non-reactive system.

Key words: drop size, tetrahydrofuran, reciprocating plate reactor

## PE-10

# THE USE OF DESIGN OF EXPERIMENTS AND RESPONSE SURFACE ANALYSIS IN CHLOROPHYLLS EXTRACTION FROM STINGING NETTLE

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Natural matrices are very complex by nature of chemical constituents. As a result of this complexity, in the general case, it is very difficult to consider the mixture component in plant matrices separately. In order to achieve an acceptable extraction rate at reasonable cost, mass transfer on analytes of interest from plant matrices at first, must be carried out with optimized phase system in which the selective mass transfer is fast and efficient. Further, the large number of influential parameters on the extraction process which are often difficult to estimate and sometimes almost impossible to measure independently or interactively, require mathematical modeling approach.

In this study, we applied tools for experimental design to study the process of chlorophylls extraction from stinging nettle matrix using maceration technique with ethanol as extraction solvent. Independent operational parameters - extraction conditions were: time in the range from 1 to 5 days, temperature at 25°C and quantity of solid and liquid phase from 2-10 g and 40-100 mL, respectively. The influence of these independent variables on the chlorophylls yield has been studied. Response surface methodology was used to predict the correlation between variables and extracted quantity of chlorophylls.

The results from the performed statistical analysis and the data obtained from the equations that adequately describe the process of chlorophylls extraction, indicate that the most influential factor in this phase system is solid and liquid phase ratio. The positive influence of the duration of extraction has been also confirmed. The data of interactive influences of independent variables confirm that there is a significant negative influence of the interaction between the quantity of solid phase and time of extraction. These results contribute to the findings that the application of the tools for experimental design enables determination of the most influential independent variables, as well as definition of the interval of change of the influential factor for achieving the desirable values of dependent variable. It appears that all the information required for the development of time-saving efficient mass transfer process can be obtained with simple mathematical model.

Keywords: stinging nettle, extraction, yield of chlorophyll, experimental design, response surface analysis

**PE-11**

**ULTRASOUND ASSISTED BIODIESEL PRODUCTION FROM  
USED COOKING OIL**

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Biodiesel usually is obtained by two step reaction of transesterification using energy extensive process. This is result to low solubility of methanol into the oil and production of glycerin as a byproduct which inhibits the reaction. The rate of the biodiesel production process is the mass transfer controlled at the first several minutes and continued to rate limiting reaction. Ultrasound assisted biodiesel production is a relatively new promising method which can be conducted in a batch or continuous conditions.

In this study, the ultrasound assisted base catalyzed reaction of biodiesel production from the used cooking oil in a batch conditions was analyzed. The effects of the most relevant variables, amount of catalyst, reaction time and the molar ratio oil/alcohol, were analyzed. Transesterification of the used cooking oil has been carried out with a molar ratio of oil to methanol 1:4.5, 1:6, 1:9 and 1:12; 0.5, 0.7 and 1.0%wt of KOH to oil, 65 °C temperature, 30 min and 60 min reaction time. The optimum conditions for this process was molar ratio of oil to methanol 1:6, using 0.70%wt of KOH and 60 min reaction time. In addition, the conventional two step 2x30 min reaction of transesterification is compared with the ultrasound assisted process.

Obtained biodiesel was methanol regenerated, dry washed, analyzed and characterized by standard test methods. The composition of methyl esters was determined using GC-MS and FT-IR spectroscopy.

Key words: biodiesel, used cooking oil, ultrasound, transesterification

## PE-12

# FAST BIODIESEL PRODUCTION IN THE PRESENCE OF VARIOUS CO-SOLVENTS

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Several processes for biodiesel production have been developed. The most of them are based on two step alkali-catalyzed reaction separating glycerin fraction between each step to increase the percent of methyl esters in a produced biodiesel. A slow dissolving rate of the oil in the methanol causes a long reaction time. Changing a two-phase reaction to a one-phase reaction through the addition of a co-solvent, generates an oil-dominant one-phase system in which the mass transfer is improved and the reaction is faster.

The aim of this work is to examine the effect of using various types of co-solvents and their amounts to the methyl ester content of obtained biodiesel. One-phase transesterification reaction of used cooking oil have been conducted at 65°C and 30°C (using diethyl ether as a co-solvent), 30 min reaction time, molar ratio of oil to methanol 6:1, at 1wt% KOH to oil, using co-solvents: tetrahydrofuran (THF), hexane, acetone, fatty acid methyl ester (FAME) and diethyl ether. The volume of used co-solvent varied as 1, 1.25 and 1.5 times volume of methanol. The obtained biodiesel was dry washed, analyzed and characterized by FT-IR and GC-MS. Biodiesel with the highest methyl ester content of 98.02 % was obtained using 1 volume of hexane as a co-solvent times volume of methanol. The major components of the biodiesel obtained from used cooking oil were methyl esters of oleic, linoleic, palmetic and stearic acid.

Key words: biodiesel, co-solvent, one-phase reaction, used cooking oil, transesterification

## PE-13

# THE PARTIAL PURIFICATION OF NATURAL COAGULANT EXTRACTED FROM COMMON BEAN ON IRA 958 CL ANION EXCHANGE RESIN: THE OPTIMIZATION OF RESIN BINDING CONDITIONS

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Coagulation and flocculation are commonly used steps in the water and wastewater treatment. They are usually conducted by adding chemicals such as salts of aluminium and iron and polyelectrolytes. Since application of these chemicals has some serious disadvantages such as a potential harmful influence of their residuals in water on human health and problems with sludge disposal, the intensive investigations of natural coagulants have been conducted in the last years in order to replace chemical coagulants in water and wastewater treatment. These coagulants are of organic nature and they can increase organic load of treated water, so they require purification in order to remove compounds that do not have coagulation activity. In this work natural coagulant was extracted from 50 g/l of ground common bean with 0.5 mol/l NaCl. Proteins from this crude extract were precipitated by adding ammonium-sulphate; the precipitate was separated from the liquid by centrifugation and dissolved in 1 ml of 0.01 mol/l phosphate buffer (pH 7). The dialysis was conducted in order to remove salt ions. Further purification was done by anion-exchange resin Amberlite IRA 958 Cl in batch process. Prior to this, the optimization of resin binding conditions was done. The kinetic of proteins binding for anion exchange resin was examined and contact time of 15 minutes was determined as optimal. Within this period of time the highest binding efficiency 88.46% was achieved at resin/protein solution ratio 1:0.5. The amount of attached protein increased with the increasing of initial protein concentration in protein solution, but binding efficiency decreased. Ionic strength of phosphate buffer did not influence significantly on binding efficiency. The best binding of proteins at resin IRA 958 Cl was achieved at pH 7.

Key words: Natural coagulants, common bean, anion exchange resin

**PE-14****INFLUENCE OF THE REACTION PARAMETERS ON THE CATALYTIC DEGRADATION OF AOR WITH OXONE OVER BULK AND SUPPORTED COBALT AND MIXED CO-Fe SPINEL OXIDES**M. Stoyanova<sup>1</sup>, St. Christoskova<sup>1</sup>, I. Slavova<sup>1</sup>, V. Ivanova<sup>1</sup>, D. Petrov<sup>2</sup>

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The current study is focused on the oxidative catalytic degradation of non-bio degradable azo-dye Acid Orange 7 (AOR) in aqueous solutions using peroxymonosulphate (PMS) as an oxidant. The process is based on the *in situ* generation of highly reactive sulfate radicals (SRs) through heterogeneously mediated activation of PMS by bulk and MgO supported cobalt and cobalt-iron spinel oxides (with Co/Fe atomic ratio of 2 and 0.5). Several factors influencing effectiveness of the AOR degradation process such as catalyst nature and amount, ratio of oxidant concentration to the dye concentration ( $C_{PMS}/C_{AOR}$ ), pH, and ultrasonic dispersion of the catalyst were investigated. It was found that all metal oxide, deposited on MgO (oxide loading of 5 wt.%) exhibited a much higher catalytic activity in sulphate radical generation and dye degradation than corresponding bulk oxides. Complete destruction of the dye chromophore structure is achieved in a short reaction period ranging from 10 minutes using  $Co_3O_4/MgO$  to 25 minutes on  $CoFe_2O_4/MgO$ . The amount of the catalyst substantially affects the reaction rate and the effect was more pronounced for the bulk catalysts. In fact, degree of dye discoloration for the first 5 minutes increased by 50% and the time for complete decolorization of the solutions was reduced 5 times by 3.5 fold increase in catalyst loading. Results also revealed that the dye removal efficiency did not increase significantly when the  $C_{PMS}/C_{AOR}$  ratio was changed from 6:1 to 10:1, however higher degree of further oxidation of intermediate products was registered. The decolorization rate considerably decreases as the solution pH increases from 4 to 9, probably due to the self dissociation of oxidant through non radical pathways. Moreover, stable intermediates containing naphthalene ring are formed during the AOR oxidation in alkaline medium, which do not undergo further destruction. Pre-treatment of the dye solution - catalyst system with ultrasound accelerates the oxidative degradation of the dye resulting from the increase in the number of active sites for PMS activation and consequently faster generation of sulfate radicals. Catalysts prepared in this work are effective for activation of PMS for the production of sulfate radicals and therefore could be potentially used for degradation of organic pollutants in wastewater.

Key words: cobalt oxides, Orange II, heterogeneous oxidation, peroxymonosulphate, sulfate radicals

**PE-15**

**ROLE OF THE SYNTHESIS METHOD ON THE CATALYTIC ACTIVITY OF  
Ni – Ce – OXIDE SYSTEMS FOR CO OXIDATION**

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In this study, bulk Ni-oxide catalytic systems were synthesized by applying an oxidation-precipitation method with reverse order of feeding the precipitator to the system. Moreover, ceria-supported nickel oxide catalysts as well as mixed Ni – Ce oxides were prepared using two different techniques: deposition-precipitation for NiO<sub>x</sub>/CeO<sub>2</sub> catalyst and method of co-precipitation of Ni – and Ce – hydroxides and subsequent heat treatment for Ni – Ce oxide catalyst, respectively. The synthesized oxide systems were characterized by means of Fourier transform Infrared spectroscopy, powder X-ray diffraction and chemical analysis, including determination of active oxygen content and surface area.

The catalytic activity of the samples towards carbon monoxide oxidation has been studied. Oxidation process was performed in flow-line equipment with an isothermal reactor with fixed catalyst layer under certain conditions. The effluents from the reactor were analyzed by on-line gas chromatograph equipped with TCD detector. Results have shown that 100% CO conversion is attained over all catalytic samples studied, however at different reaction temperature. Best catalytic performance in the studied reaction demonstrated catalytic systems in which the active phase of NiO<sub>x</sub> is deposited on CeO<sub>2</sub>. The comparison of activity data for bulk and ceria-supported catalysts confirms that CeO<sub>2</sub> support significantly influences catalytic activity of the samples in the gas-phase CO oxidation which results in a significant decrease of the reaction temperature (about 60°C) for complete CO conversion.

*Keywords:* CO, complete oxidation, Ni – and Ni-Ce- oxide systems.

## PE-16

# FRUIT JUICES PRODUCTION IMPACT ON THE ENVIRONMENT - FLOW MODEL

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Wastes from the food production are organic substances which occur during the processing of agricultural raw materials into finished food products. This material often contains ingredients that can be used in some way. In this case, instead of the term „waste“ it is correctly to use the term „by-product“, which emphasizes market value of the waste.

Processing of by-products from food industries, using the classic method of waste disposal, it is rarely implemented, due to the low market value of products produced during the incineration and composting and emissions of harmful gases (SO<sub>2</sub> and nitrous oxides).

New methods in process engineering provide us with new and very useful products from waste products of food industry and agriculture. The new methods focus on a particular ingredient in the food by-products. For example, cellulose fibers and pectin (from Spent grains, apples, tomatoes, peels of citrus fruits and carrots processing by-products), after extraction and processing can be used in human and livestock nutrition in the form of substances of high nutritive value.

Cellulosic materials can be converted into biogas by anaerobic process of fermentation

Isolation of biologically active compounds from materials generated as waste during the processing of raw materials of plant and animal origin was more prominent in the food industry, but also in the pharmaceutical, cosmetic and other industries.

In the paper, authors carried out the analysis of fruit juices production impact on the environment, using different techniques: flow model, process model, the monetary model and risk assessment. The aim of this analysis was to determine the actual environmental impact of production of juices and finished goods, if the waste and by-products, resulting in the process, are used for making various kinds of new products. Analysis included various inputs in the processing (3 types of fruit, individually and in various combinations, other raw materials and packaging) and different outputs. Economic analysis of each procedure was performed.

**Keywords:** fruit juices, by-products, impact on environment

**PE-17**

**DETERMINATION OF THE OPTIMAL PROCESS REGULATOR  
PARAMETERS FOR THE SYSTEM OF ACTIVATED SLUDGE  
WASTEWATER TREATMENT**

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The principal objective of wastewater treatment is generally to allow human and industrial effluents to be disposed of without danger to human health or unacceptable damage to the natural environment. Activated sludge wastewater treatment is based on the utilization of microorganisms (bacteria) to naturally degrade organic waste resulting in BOD reduction, COD reduction and wastewater odor control.

The studied activated sludge system refers to a wastewater treatment plant, whose volume is  $V=80\text{m}^3$ , volumetric flow of wastewater  $Q = 4 \text{ m}^3/\text{h}$ , saturation constant of Monod  $K_s= 2500 \text{ COD ( mg O}_2 / \text{l )}$ , concentration of substrate in the inlet stream  $C_{sv}= 150 \text{ COD}$ , maximal specific speed of biomass growth  $\mu_m = 0.02 \text{ h}^{-1}$ , biomass concentration  $C_x = 6.1 \text{ g (d.m.)/l}$  and coefficient of substrate's biomass yield  $Y_{x/s} = 0.025$ .

The aim of this article is the determination of the optimal process regulator parameters for the system of Activated sludge wastewater treatment. For realization of this point, the mathematical model and total transfer function was created. The system was analyzed in closed-loop configuration through application of PID regulator. By using of software MATLAB/Simulink, the dynamic simulation for the investigated biological treatment process was done. Through application of transient responses, optimal regulator parameters ( $K_C$ ,  $\tau_I$ ,  $\tau_D$ ) were determined.

**Keywords:** PID regulator, Activated sludge system, transient responses

**PE-18**

**GREEN SOLVENT EXTRACTION OF FRAGRANCE COMPONENTS FROM  
*OCIMUM BASILICUM L.***

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The purpose of this research study is to analyze the possibility of application of the alternative extraction techniques in isolating high-purity fragrance components present in the plant material used – *Ocimum Basilicum L.* The dominant organic volatiles – constituent components of the basil plant matrix were found to be *linalool*, *methyl-chavicol* and *1.8-cineol*.

The idea of green solvents expresses the goal to minimize the environmental impact resulting from the use of solvents in chemical production. These processes are optimized in order to produce maximal profitability with minimal environmental impact. Non-conventional separation procedure - supercritical fluid CO<sub>2</sub> extraction (SFE-CO<sub>2</sub>) conforms to the strict demands of the precise process eco-technologies. It represents a perspective method especially in obtaining eco-friendly extracts from vegetable and animal raw materials. Implementation of SFE-CO<sub>2</sub> as a green solvent, for isolation of vegetable extracts results in obtaining high quality and high purity total extract and excludes the presence of organic solvents, heavy metals and some microorganisms.

This work investigates the effects of process parameters such as extraction pressure, temperature and extraction time on SFE-CO<sub>2</sub> extraction process, while the flow rate of supercritical CO<sub>2</sub> and the plant particle size were kept constant. Gas chromatography – mass spectrometry technique was used to qualitatively identify the fragrance components as well as for a quantitative determination of the yield as a function of different operating conditions.

**Keywords:** *Ocimum basilicum L.*, green solvent extraction, fragrance components

**PE-19****IMPACT OF THE BINDER TYPE AND GRANULATION METHOD ON THE PARTICLE SIZE OF ALPHA LIPOIC ACID GRANULES**

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Alpha lipoic acid is an antioxidant substance which is created in the human body and has a unique activity towards free radical scavenging. Alpha lipoic acid protects the human organism from the free radicals in both intra- and extra-cellular manner, while the other types of antioxidants act only intra-cellularly. By getting older the human organism is less capable to create Alpha lipoic acid and this is the reason why this substance should be supplied from the food and food supplements. The most important source of Alpha lipoic acid is the red meat. Smaller amounts of this antioxidant could be also found in products such as potatoes, broccoli, tomato, spinach. The reduced type of Alpha lipoic acid stimulates the activity of vitamin C and E towards regeneration of reduced antioxidants, stimulates the activity of coenzyme Q10, and also promotes cell detoxication and regeneration. The unique activity of Alpha lipoic acid is due to its solubility in both water and lipids and the capability to pass through all body membranes including blood-brain barrier.

Pure Alpha lipoic acid demonstrates very specific properties such as small particle size, bad flowability, low melting point ( $\approx 40^\circ\text{C}$ ), sticking etc. These properties make Alpha lipoic acid very hard to formulate into tablets and capsules. One of the possible solutions for improving the flowability and decrease the sticking phenomena is to granulate the Alpha lipoic acid to obtain granules which could be easily compressed into tablets or filled into capsules. Granulation is process of agglomeration of very fine particles into larger groups-agglomerates in purpose to improve their physic-chemical properties and bioavailability, to reduce substance loss and to prevent spreading of some toxic substances. There are two main types of granulation techniques, wet and dry. In the case of wet granulation, the agglomeration of fines is made in presence of binding compound and granulation solvent/liquid (mostly water). Wet granulation could be done in several devices such as, High- and Low-Shear mixers, Fluid bed granulator, Spray drier etc.

The purpose of this article is to compare the size of granules made from Alpha lipoic acid and three different types of binders, which are produced in two different wet granulation devices (High shear and Fluid bed device), and to determine how the granule size impacts the solubility of this potent antioxidant.

**Key words:** Alphalipoic acid, granulation, binders, particle size

## PE-20

# PROCESS MONITORING OF ANAEROBIC DIGESTION OF ORGANIC SOLID WASTE IN A LABORATORY BATCH BIOREACTOR

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Composting is an important process in which organic materials are biodegraded by microorganisms, resulting in the production of a uniform organic material, which can be utilized as a fertilizer in agriculture.

For our study, we have selected animal manures as raw substrate organic material, and we have conducted a study of composting and digestion experiments at a set up laboratory scale bioreactor. Physico-chemical parameters were determined during the process and their accurate control was achieved.

In case of using as substrate only animal manures, Fourier Transform Infrared Spectroscopy was used to study the organic matter decomposition in this organic waste materials. These investigations provided detailed information about transformation in chemical composition and their behavior during entire the composting process. The FTIR spectra revealed an increase in aromaticity and a decrease in carbohydrates.

**Key words:** *manure composting process, bioreactor, parameter monitoring, FTIR analyzing*



**SPECTROSCOPY AND STRUCTURAL CHEMISTRY (SS)**

## SS-1

### IR AND RAMAN SPECTRA OF 3-AMINOPROPYLTRIMETHOXYSILYL – MODIFIED SILICA GEL

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3-Aminopropyltrimethoxysilane is a molecule with two functional groups that can be used as spacer (coupling agent), particularly on silica gel [1, 2]. Its methoxy group reacts with the –OH groups from the silica gel resulting in a siloxy linkage. The amino group is then accessible for further coupling to molecules, e.g., transition-metal complexes for applications as heterogeneous catalysts [3].

Employed were absorption and diffuse reflectance IR techniques, together with MicroRaman technique to follow the changes in the spectra of silica-gel before and after the chemisorption of APTMS on its surface. Attachment of molecules possessing catalytic properties is also investigated and proved to occur on a previously modified surface of silica-gel. An indicator that chemisorption of APTMS molecules on the silica-gel surface occurred is the observation of the lowering in the intensity of the absorption band in the OH stretching region. Comparison of the IR and Raman absorption bands in the CH<sub>2</sub> stretching region with published data [4] indicates that complete substitution under the experimental conditions has occurred. The comparison of the recorded Raman spectra with literature data [5, 6] and the performed non-linear curve fitting indicate the possible band due to the newly formed siloxy bond.

Keywords: 3-Aminopropyltrimethoxysilane; Modified Silica-gel; IR and Raman spectra

**SS-2**

**MODEL DIELECTRIC FUNCTIONS EXPLAINING EVANS HOLES IN THE  
REFLECTANCE SPECTRA OF POTASSIUM HYDROGEN SUCCINATE  
SINGLE CRYSTAL**

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Reflectance spectra may show very different and interesting shapes. The most interesting may be connected to Evans holes. Model calculations to reproduce this effect were done applying model dielectric functions. When a weak oscillator appears within the frequency region of a strong one (i.e. between its TO and LO frequencies), its LO-mode frequency shifts towards higher wavenumbers. As a consequence, the oscillator strength of the corresponding weak mode becomes negative which produces a dip (Evans hole) in the reflectance spectrum. This model was successfully applied to analyze polarized reflectance spectra of potassium hydrogen succinate single crystal in the ac crystal plane. The crystal symmetry was described by phenomenological model and by full symmetry consideration. Both approaches describe all basic spectral features, the wide reflectance of  $\nu_{as}(\text{OH})$  and the two Evans holes appearing on its shoulder [1].

Key words: Dielectric model function; Evans holes; Tutton salts, Potassium hydrogen succinate single crystal

## SS-3

**ELECTRON CONFIGURATION OF (SOME) CO-ORDINATION  
COMPOUNDS OF MO(VI) WITH AMINO ACIDS**Victoria Trifonova, Krasimir Vassilev

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Quantum-chemistry calculations and analysis of the electron configuration of transition metals co-ordination compounds allow elucidating the origin of their physical and chemical properties at electron level, as well as predict some of substance properties. This is necessitated mostly due to their use in catalysis and the basic role they play in biological processes.

For this purpose, the geometry was optimized and the electron structure of the Mo(VI) co-ordination compounds with some amino acids – MoO<sub>2</sub>(Gly)<sub>2</sub>, MoO<sub>2</sub>(Ala)<sub>2</sub>, MoO<sub>2</sub>(Cys)<sub>2</sub>, MoO<sub>2</sub>(Met)<sub>2</sub>, MoO<sub>2</sub>(Phe)<sub>2</sub>, MoO<sub>2</sub>(Tyr)<sub>2</sub>, MoO<sub>2</sub>(Arg)<sub>2</sub>, MoO<sub>2</sub>(Gly)<sub>2</sub> was calculated. All the calculations were performed using the semiempiric quantum-chemistry method ZINDO/1 from the software package HyperChem 5.1, using the standard parametrization for molybdenum atom. The structures were preliminarily optimized using the molecule mechanics of the same software package. The bond lengths in co-ordination compounds were calculated. For comparison, the results obtained from *ab initio* calculations for MoO<sub>2</sub>(Gly)<sub>2</sub> carried out with a minimum of basic functions STO-3G for all atoms, as well as data from the X-ray analysis of structurally close complex MoO<sub>2</sub>(2-o-hydroxybenzimidazole)<sub>2</sub>. The result showed that the geometry obtained from the calculations correctly reveals the special features – bonds in *trans* position with respect to the ligand multiplicity were longer than these in *cis* position. The bond lengths metal–ligand (Å) of the co-ordination ligands with Mo(VI) were calculated with representatives of the amino acids. Bond lengths were found to be identical in the different compounds. The analysis of the population in molybdenum atomic orbitals defines electron configuration  $4d^{3.85}5s^{0.42}5p^{1.15}$  of the valent electron layer. The co-ordination compounds obtained were studied as catalysts in the reaction of cyclohexene oxidation with *tert*-butylhydroperoxide with the highest activity being observed for MoO<sub>2</sub>(Gly)<sub>2</sub> while the lowest – for MoO<sub>2</sub>(Tyr)<sub>2</sub>.

Key words: molybdenum, complexes, oxidation.

**SS-4****PHONON CONFINEMENT IN CADMIUM SELENIDE QUANTUM DOT SOLIDS SYNTHESIZED BY CONVENTIONAL AND SONOCHEMICAL ROUTES: A RAMAN SCATTERING STUDY**

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Cadmium selenide quantum dot solids, deposited in form of thin films, were synthesized by conventional template-free chemical and sonochemical routes. Sonochemical synthesis was performed applying high-intensity ultrasonic irradiation to the reaction system. A direct immersion ultrasonic horn generating continuous-wave ultrasound with frequency of 20 kHz and intensity of  $100 \text{ W cm}^{-2}$  was used for sonification. Raman scattering technique was used to study the phonon confinement effects in the synthesized low-dimensional materials. Raman spectra were recorded using micro-Raman spectrometer, LabRam 300 (Horiba Jobin-Yvon), equipped with frequency doubled Nd:YAG laser operating at 532 nm with the excitation power around 5 mW at the sample. X-ray diffraction technique for polycrystalline samples was used to characterize the composition and structural properties of the synthesized materials (average crystal size, lattice constants, lattice strain and dislocation densities). Band gap energies were calculated on the basis of the spectral dependencies of absorption coefficients of the synthesized films. These were constructed from the measured UV-VIS spectra, employing the parabolic approximation for the dispersion relation with a combined interpolation-extrapolation technique.

The LO phonon band in the Raman spectra of QD solids exhibits notable red-shift in comparison to the value characteristic for the corresponding bulk material along with an enhancement of its half-width. A pronounced asymmetry on the low-frequency side of the band due to the one-phonon LO mode is observed. These effects were generally attributed to the relaxation of  $k = 0$  selection rule due to the finite dimensions of the nanocrystals (*i.e.* phonon confinement effects) and structural imperfections. Appearance of a low-frequency shoulder of the LO band was attributed to surface optical phonon (SO) or zone-edge phonon (ZE) modes. Besides the fundamental LO band, several overtones of this transition were clearly observed as well. The TO phonon band could be resolved only with non-linear interpolation techniques. The observed trends in all of the mentioned features related to the LO phonon band in the case of materials synthesized by conventional and sonochemical routes are in line with the results from the structural and optical studies.

Key words: cadmium selenide, quantum dots, quantum dot solids, semiconductors, phonon confinement effects

**SS-5****SIZE DEPENDENT PROPERTIES OF  
THIN FILMS COMPOSED BY CLOSE-PACKED  $\text{CuInS}_2$  QUANTUM DOTS**

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Thin films of close-packed  $\text{CuInS}_2$  quantum dots were synthesized using template-free conventional chemical route as well as sonochemical approach. Sonification was carried out applying high-intensity continuous-wave ultrasound irradiation by direct immersion of ultrasonic horn in the reaction system. The developed routes allow deposition of phase pure chalcopyrite  $\text{CuInS}_2$  with pronounced nanocrystalline structure. Heterogeneous sonochemical effects support additional crystal size decrease in comparison to the conventional approach.

The structural and optical properties of the title thin film material were studied with a special emphasis on their dependence on the crystal size. The evolution of crystal size and lattice strain relaxation upon coalescence processes, induced by thermal annealing were followed by X-ray diffraction measurements. For these purposes, detailed studies of the shapes of XRD peaks along with the analyses of the  $b^2 \cos^2 \varphi$  vs.  $\sin^2 \varphi$  plots were carried out. Refinement of the lattice constant values, carried out by multiple regression analysis techniques, showed an increasing trend of these parameters upon annealing, which eventually approach the bulk values. These data have therefore supported the trend of lattice strain relaxation upon annealing.

In addition, the nanostructure of synthesized thin film material was confirmed by AFM measurements. This technique was also used to investigate the morphological characteristics and surface roughness of studied samples.

Optical band gap energy of the films was determined from the spectral dependence of the absorption coefficient, constructed on the basis of measured transmission spectra of chemically and sonochemically synthesized materials. Optical absorption data were analyzed in the framework of parabolic approximation for the dispersion relation, implementing a combined interpolation-extrapolation technique. Calculated band gap energies are blue-shifted compared to the bulk value – which lies at red edge of the solar spectrum, making the synthesized thin films potential effective light-absorbing materials for solar cells applications. Ultrasonic irradiation of the reaction system results in a larger blue shift of absorption edge indicating the possibility for further control of the optoelectronic properties of this material by sonochemical approach. Upon coalescence processes, induced by thermal annealing, optical  $E_g$  values exhibit red shifts, finally approaching the corresponding bulk values.

Keywords:  $\text{CuInS}_2$ , quantum dots, semiconductors, confinement effects, sonochemistry

## SS-6

**THE ACIDITY OF SURFACE-EXPOSED LEWIS SITES IN PARTIALLY  
FLUORINATED MICROCRYSTALLINE  $\gamma$ -ALUMINA: A QUANTUM  
CHEMICAL CLUSTER MODEL STUDY**Irena Nastova<sup>1</sup>, Tomaž Skapin<sup>2</sup>, Ljupčo Pejov<sup>1</sup>

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The influence of partial fluorination of microcrystalline  $\gamma$ -alumina on the acidity of surface-exposed Lewis sites was studied by quantum chemical cluster model approach, using pyridine as a test-probe molecular system. B3LYP/6-31++G(*d,p*) and HF/6-31++G(*d,p*) levels of theory were employed, considering the standard and counterpoise-corrected potential energy surfaces (PESs) of pyridine attached to finite clusters modeling the surface, focusing primarily on the non-polar (100) and (110) crystal planes of the pure and partially fluorinated  $\gamma$ -alumina. Neutral cluster models representing the non-polar (100) and (110) planes were derived from the crystal structure of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Termination of the clusters at the bulk-cluster interfaces was performed by OH groups or HOH molecules. Partial fluorination was achieved by replacing some of the OH groups with fluorine atoms. Both the standard and the counterpoise-corrected potential energy surfaces of free pyridine, pyridine-Al(OH)<sub>x</sub>(H<sub>2</sub>O)<sub>y</sub>, as well as pyridine-Al(OH)<sub>x</sub>(H<sub>2</sub>O)<sub>y</sub>F<sub>z</sub> clusters in the ground electronic state were explored at the above-mentioned levels of theory. Explicit inclusion of dynamical electron correlation effects along with the elimination of the basis set superposition effects in geometry optimization and harmonic vibrational analysis were found to be crucial to reproduce the experimental trends in the shifts of the pyridine  $\nu_{19b}$  and  $\nu_{8a}$  modes upon fluorination. As compared to the case of pure  $\gamma$ -alumina, the acidity of surface-exposed Al-sites was found to increase upon fluorination. This is manifested through a ~ 10 % increase of the interaction energies, and also through the characteristics of the electronic density and density Laplacian at the intermolecular bond critical points. Bader analysis of the electronic density has shown that pyridine adsorption on pure and fluorinated  $\gamma$ -alumina can be classified as a typical non-covalent interaction.

Key words: pyridine, adsorption, gamma-alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), fluorinated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Lewis adsorption sites

## SS-7

**ANHARMONIC VIBRATIONAL FREQUENCY SHIFTS UPON  
INTERACTION OF PHENOL(+) WITH THE OPEN SHELL LIGAND O<sub>2</sub>.  
THE PERFORMANCE OF DFT METHODS VERSUS MP2**

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*Anharmonic* vibrational frequency shifts of the phenol(+) O-H stretching mode upon complex formation with the open-shell ligand O<sub>2</sub> were computed at several DFT and MP2 levels of theory, with various basis sets, up to 6-311++G(2df,2pd). It was found that all DFT levels of theory significantly outperform the MP2 method with this respect. The best agreement with the experimental frequency shift for the hydrogen-bonded minimum on the potential energy surfaces was obtained with the HCTH/407 functional (-93.7 cm<sup>-1</sup> theoretical vs -86 cm<sup>-1</sup> experimental), which is a significant improvement over other, more standard DFT functionals (such as, e.g. B3LYP, PBE1PBE), which predict too large downshifts (-139.9 and -147.7 cm<sup>-1</sup> respectively). Good agreement with the experiment was also obtained with the mPW1B95 functional proposed by Truhlar *et al.* (-109.2 cm<sup>-1</sup>). We have attributed this trend due to the corrected long-range behavior of the HCTH/407 and mPW1B95 functionals, despite the fact that they have been designed primarily for other purposes. MP2 method, even with the largest basis set used, manages to reproduce only less than 50 % of the experimentally detected frequency downshift for the hydrogen-bonded dimer. This was attributed to the much more significant spin-contamination of the reference HF wavefunction (compared to DFT Kohn-Sham wavefunctions), which was found to be strongly dependent on the O-H stretching vibrational coordinate. All DFT levels of theory outperform MP2 in the case of computed anharmonic OH stretching frequency shifts upon ionization of the neutral phenol molecule as well. Besides the hydrogen-bonded minimum, DFT levels of theory also predict existence of two other minima, corresponding to stacked arrangement of the phenol(+) and O<sub>2</sub> subunits. mPW1B95 and PBE1PBE functionals predict a very slight blue-shift of the phenol(+) O-H stretching mode in the case of stacked dimer with the nearly-perpendicular orientation of oxygen molecule with respect to the phenolic ring, which is entirely of electrostatic origin, in agreement with the experimental observations of an additional band in the IR photodissociation spectra of phenol(+)-O<sub>2</sub> dimer [Patzner, A.; Knorke, H.; Langer, J.; Dopfer, O. *Chem. Phys. Lett.* **2008**, *457*, 298]. The structural features of the minima on the studied PESs were discussed in details as well, on the basis of NBO and AIM analyses.

Key words: phenol radical cation, O-H stretching mode, non-covalent intermolecular interactions, density functional theory, open-shell ligands

**SS-8**

**THEORETICAL AND EXPERIMENTAL STUDY OF THE VIBRATIONAL  
SPECTRA OF HORNESITE,  $Mg_3(AsO_4)_2 \cdot 8H_2O$  AND SYMPLESITE,  
 $Fe_3(AsO_4)_2 \cdot 8H_2O$**

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The arsenate water-bearing minerals hornesite (Alšar, Macedonia) and symplesite (*Laubach Mine*, Germany) were studied with vibrational spectroscopic (IR and Raman) and quantum theoretical methods. The observed vibrational spectra in the higher (1100–600  $cm^{-1}$ ) and especially lower (600–450  $cm^{-1}$ ) frequency region of  $AsO_4$  vibrations could clearly discriminate between the studied minerals. The differences between their crystal structures are much pronounced in IR water-bending and water-stretching regions. Essentially, the bands in the IR and Raman experimental spectra were tentatively assigned. To support the tentative assignment of bands in the vibrational spectra of the mentioned minerals, periodic DFT calculations were carried out. Geometry optimizations of the 3D periodic systems were carried out and subsequently to geometry optimization, numerical harmonic vibrational analysis was performed, computing the dynamical matrix by numerical evaluation of the first-derivative of the analytical atomic gradients. In most cases, the assignments were either supported or implied by the obtained theoretical data. It is worth mentioning that this is the first experimental and theoretical study of the vibrational spectra of the very-rare symplesite mineral.

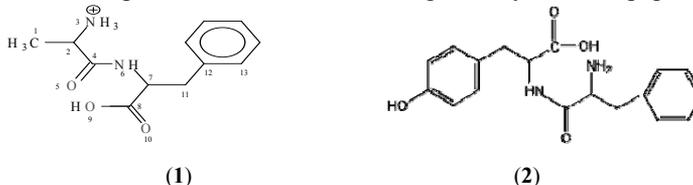
Keywords: hornesite; symplesite; IR; Raman; quantum theoretical methods.

## SS-9

## SYNTHESIS AND SPECTROSCOPIC ELUCIDATION OF AROMATIC PEPTIDES

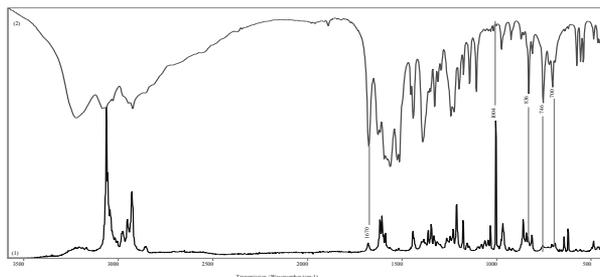
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The aromatic dipeptides L-phenylalanyl-L-tyrosine (*H-Phe-Tyr-OH*) and the hydrochloride of L-alanyl-L-phenylalanine stabilized as monohydrate (*H-Ala-Phe-OH.HCl.2H<sub>2</sub>O*) are synthesized and studied. The linear-polarized spectroscopy (IR- or Raman) of oriented colloids in nematic host coupled with advanced theoretical calculations are applied as a part of modern approaches for spectral and structural elucidation of small aromatic peptides. We choose these examples with a view to compare the scopes and limitations of the polarized vibrational tool, studying the IR- and Raman spectra as well as ones of the widely used theoretical methods for prediction of the molecular geometry of small peptides.



Structure of the studied dipeptides: H-Ala-Phe-OH (1) and L-phenylalanyl-L-tyrosine (2)

In these examples as well as in other aromatic peptides, the characteristic IR-bands of  $\text{NH}_3^+$ -group, typical for zwitterionic and protonated peptides, such as  $\nu^{\text{as}}_{\text{NH}_3^+}$ ,  $\delta^{\text{as}}_{\text{NH}_3^+}$ ,  $\delta^{\text{as}'}_{\text{NH}_3^+}$ , are low-intensive in corresponding Raman spectra. The bands between  $3100\text{--}2500\text{ cm}^{-1}$  ( $\nu^{\text{as}}_{\text{NH}_3^+}$ ,  $\nu^{\text{s}}_{\text{NH}_3^+}$ ), at  $1681\text{ cm}^{-1}$  ( $\delta^{\text{as}}_{\text{NH}_3^+}$ ) in *H-Phe-Tyr-OH* which are observed in the IR-spectrum, are low-intensive or/and disappeared in corresponding Raman spectrum. The same is valid for  $\nu_{\text{C=O}}$  (Amide I) and  $\nu_{\text{C=O}}$  (COOH) stretching vibrations. The obtained results, especially for the characteristic IR-bands of amide  $\text{C=O-NH}$  fragments and out-of-plane vibrations of the aromatic residues provide a structural information about the configuration of amide  $\text{O=C-NH}$  group/s and corresponding amide planes in the peptide molecules, which are characterized with a large number of vibrations. The main advantages of the applied approach based on linear-polarized vibration spectroscopy are the ability to provide local structural information in solid state of the aromatic peptides, independent of their amorphous or polycrystalline character.

Raman (1) and IR-(2) spectra of dipeptide *H-Phe-Tyr-OH* in solid-state

**Key words:** aromatic peptides; L-phenylalanyl-L-tyrosine (*H-Phe-Tyr-OH*), (*H-Ala-Phe-OH.HCl. 2H<sub>2</sub>O*); linear-polarized spectroscopy.

**TEXTILE ENGINEERING (T)**

## T-1

### **SYNTHESIS OF POLY (ACRYLAMIDE)-STARCH AS A POTENTIAL SIZE BASE MATERIAL IN SIZING OF YARNS FOR WEAVING**

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Potato starch was hydrolyzed with HCl to obtain starch with different molecular weights. Different concentrations of acrylamide were grafted onto hydrolyzed starches in the presence of potassium permanganate/citric acid as an initiator. The newly synthesized products were used as sizing agents of cotton yarns to test their suitability for temporary improvement of physico-mechanical properties.

With the increase of the potassium permanganate concentration the graft yield of copolymerization increased and then drop off; (b) increased by increasing the acrylamide concentration within the range studied.

The molecular weights of copolymers were investigated by high-performance liquid chromatography (HPLC). Mean molar mass and molar mass distributions were determined by gel permeability chromatography Agilent 1100 Series GPC where the detector is used as a differential refractometer (RID detector) 1200 Series.

After chromatography of an appropriate sample of copolymer, depending on the used detector (RID or DAD), ChemStation software depending (RID or DAD) provides the corresponding chromatograms with typical chromatographic parameters. The program enables the activation of GPC software and transfer data obtained chromatograms for processing and analysis of molecular weight of each separated fraction of the analyzed polymers.

It was found that the molecular weight of the grafted starch directly affects the rheology and the behavior of the solution (sizing agent), the efficiency of the process of sizing the yarn and then the safety and reliability of the process of weaving.

On the other hand, physico-mechanical properties of cotton textiles, such as tensile strength, elongation at break and abrasion resistance, were found to be highly enhanced with the copolymers derived from hydrolyzed starches used as size base materials: while worse textile properties were found when the original starch was used as a sizing agent.

Keywords: starch, acrylamide, grafting, chromatography, molar mass, sizing, yarns.

## T-2

# APPLICATION OF STARCH-ACRYLAMIDE COPOLYMER IN THE PROCESS OF COTTON YARNS SIZING

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Cotton yarns are sized with a strengthening adhesive-like material (usually starch or a starch-based material), to prevent damage during the weaving process. Size is usually applied to the warp yarns, particularly susceptible to mechanical strains during weaving. In this work a newly tailored polymeric starch-derived products from potato are applied in sizing of rotor spun cotton yarns with linear density of 30 tex. Testing the suitability of these polymeric materials as sizing agent of cotton yarns was also done.

With the increase of the starch concentration to a certain value, the starch adds-on the yarns almost proportionally increased and then decreased with further increase of concentration.

Higher or lower concentrations of starch do not increase proportionally starch add-on, so the concentration of 10 % could be "ideal" for yarn sizing. The concentration of 20 % gives a slightly higher add-on than that obtained with 10 % active substance.

Tensile strength at break depends on treatment conditions, and it increased with the increase of the concentration of sizes. Therefore, tensile strength depends directly on the quantity of applied starch. Moreover, it was found that elongation at break also increased with the increase of the concentration of active components, though slightly lower, indicating that higher values of breaking strength may be due to higher additional elasticity of yarns.

An expected appropriate shrinking percentage appeared, depending on starch type and concentration, related to relaxation of stretched ends and swelling tendency. Increase of starch concentration as well as type of starch caused an increase of shrinking percentage.

Finally, it seems that the treatment with grafted potato starch shows good results regarding side and achieved effects. Additional investigations, as are other procedures, treatment conditions, new agents, may contribute in improving treatment effects relating to process shortening and simplification.

Keywords: starch, acrylamide, grafting, sizing, yarn, tensile strength, elongation at break.

**T-3**

**INFLUENCE OF THE GROUND FABRIC ON THE MECHANICAL  
PROPERTIES OF FACE-TO-FACE WOVEN VELVET**

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Woven velvets occur in every segment of the textile market: clothing, automotive industry, decorative textiles, transport, and special fabrics. The mechanical properties of the ground fabric in velvets used for upholstery are especially important, as the ground fabric bears the fabric strength, durability, and the ease of manipulation during upholstering. This research deals with the ground fabric of face-to-face woven velvets, in particular the influence of ground fabric design variations on the fabric's mechanical properties.

In the experimental part four upholstery velvet samples with different interlacing of the ground warp and weft were taken. The fabric design for the ground fabric employed weaves with ground warp floats of one, two and three yarns on the back of the fabric. For samples 1, 2 and 3 the loop was W-shaped, whereas for sample 4 it was V-shaped. For each fabric sample the examined structural parameters were: ground warp, pile warp and weft count, warp crimp, separated for the tight and lightly tensioned warp, the pile warp crimp, the weft crimp and the proportion of ground warp in the fabric. The examined physical and mechanical properties of the fabrics were: fabric strength, extension, burst strength, burst deformation height, abrasion resistance on the fabric face and back, and fabric weight.

The research shows that the strength properties of face-to-face woven velvet for upholstery purposes depend on the structural characteristics of the ground fabric (warp and weft count). Increase of the fabric density improves these properties. When examining the ground fabric weave design it is noticeable that these differences cannot be explained by treating the ground fabric as a plain structure. On the contrary, when choosing fabric design the positioning of wefts due to the influence of the tight ground warp must be carefully considered in order to obtain velvets with the best performance.

Keywords: face-to-face woven velvet, mechanical properties of velvet, velvet fabric design

T-4

## COMPARISON OF OBJECTIVE AND SUBJECTIVE FASHION INNOVATIVENESS

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Fashion is a key concept underpinning the success of clothing products. The rapid change of fashion trends forces producers to develop quick response solutions in order to satisfy market demand, treating fashionable clothes as perishable goods. Therefore, evaluations of the fashion innovativeness of a market gain importance. Such evaluations are typically conducted by measuring consumers' self-perceptions, rendering completely subjective results. The aim of this investigation is to determine if the subjective evaluation of fashion innovativeness and the objective knowledge of fashion trends correlate, on the Macedonian market.

The research was conducted on a sample of 100 participants, in the age bracket of 18 to 25 years. A domain-specific fashion innovativeness scale was used to determine the participants' subjective evaluation of fashion innovativeness. To determine the respondents fashion innovativeness objectively, panels depicting fashion trends across several categories (trousers, skirts, blouses, jeans, colours) were created. Fashion forecasts and fashion forecast archives were used to select styles and colors matching different stages of the fashion innovativeness cycle in each of the selected categories. Objective fashion innovativeness was measured through two parameters – trend awareness and propensity to wear new trends. A chi-square test was used throughout the research in order to confirm statistically significant differences among respondents in the five groups of the fashion innovativeness cycle (innovators, early adopters, early majority, late majority, laggards).

The results showed that with the examined sample the subjective fashion innovativeness curve was skewed from normal distribution towards innovative behaviour, with innovators and early adopters comprising 59% of the examined population. No correlation was found between the subjectively and objectively measured fashion innovativeness. On the contrary, when measuring fashion innovativeness through trend awareness and propensity to wear new trends the fashion innovativeness curve was skewed towards late majority; with mode values of 47% and 48% of respondents belonging to this group, accordingly. However, a correlation exists between trend awareness and the propensity to wear new trends. This indicates that the examined population will tend to wear trends they find fashionable, even though those fashion trends are already declined on the global market. The results should be carefully considered when producing clothes for the Macedonian market.

Keywords: clothing, fashion innovativeness

**T-5**

**THE ANALYSIS OF DOUBLE INTERLOCK FABRIC IMPORTANT FOR  
THERMO-PHYSIOLOGICAL COMFORT OF CLOTHING**

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Thermo-physiological comfort of clothing is referring to the comfort conditional on the optimal transfer of heat and water vapour from the skin surface, through textile in the environment. Clothing made of knitted fabrics has significant impact on thermo-physiological comfort. In previous studies a lot of attention was devoted to the thermo-physiological comfort of clothing made of single knitted fabrics. Double knitted fabrics fall into the category of new products, and literature data show that they have not been tested so far. Three samples of double interlock fabric with the same fiber composition Co/PES, the same structure but different weight per unit area and two samples of classic interlock single knitted fabric of 100% PES, with the same structure but different weight per unite are selected for testing the thermo-physiological comfort of clothing. The weight per unit area, stich density, water vapour permeability, air permeability, penetration strength and elongation were tested. Water vapour permeability, air permeability and penetration strength ware tested on both side of the knitted fabric.

Key words: thermo-physiological comfort of clothing, interlock knitted fabric, double knitted fabric, water vapour permeability, air permeability

## T-6

### SELECTIVE OXIDATION ON DIFFERENT PRETREATED COTTON YARNS

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During the production and processing of cotton cellulose fibers they are modified both chemically (oxidation and hydrolysis) and structurally (mercerization). The purpose of these modifications is to change cotton fiber reactivity (number and location of functional groups) while preventing or at least minimizing degradation. Chemical modification using selective and non-selective oxidizing agents is a useful method widely used in cellulose chemistry.

Cotton yarns used in this experiment were differently scoured by alkaline, or enzymatic (alkaline or acid pectinase) processes, mercerized-differently scoured and differently scoured-mercerized. Differently pretreated yarns were subjected to selective oxidation with periodate to cleave the 2,3-vicinal diol of the anhydroglucose units and induce aldehyde groups.

On differently pretreated cotton yarns degree of mercerization through barium activity number, FTIR-ATR ratios and dynamic (sonic) modulus were followed. Aldehyde groups introduced during oxidized of cotton yarns were determined through iodometric titration while carboxyl groups by methylene blue sorption. Degradation of oxidized cotton yarns was analyzed by lost in tensile strength, elongation and work of rupture, CIE whiteness and CIELab coordinates.

Oxidized yarns showed lower tensile strength, elongation and work of rupture, CIE whiteness and  $a^*$  and  $b^*$  values, compared to unoxidized yarns.

Selective oxidation introduced aldehyde groups with small degradation of oxidized cotton yarns.

Key words: selective oxidation, cotton yarns, structural properties, aldehyde groups, degradation

T-7

## NON-SELECTIVE OXIDATION ON DIFFERENT PRETREATED COTTON YARNS

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During the production and processing of cotton cellulose fibers they are modified both chemically (oxidation and hydrolysis) and structurally (mercerization). The purpose of these modifications is to change cotton fiber reactivity (number and location of functional groups) while preventing or at least minimizing degradation. Chemical modification using selective and non-selective oxidizing agents is quite a frequent procedure in cellulose chemistry. Non-selective oxidation with perchloric acid does not cause the cleavage of 1,4- $\beta$ -glycosidic bonds, and no reduction in chain length occurred as well as gives carboxyl groups at C6.

Cotton yarns used in this experiment were alkaline, enzymatic (alkaline or acid pectinase) scoured, mercerized-differently scoured and differently scoured-mercerized. Differently pretreated yarns were subjected to non-selective oxidation with perchloric acid.

On differently pretreated cotton yarns degree of mercerization through barium activity number, FTIR-ATR ratios and dynamic (sonic) modulus were followed. Carboxyl groups introduced in oxidized cotton yarns were determined using standard complexometric titration, calcium-acetate method and methylene blue method. Degradation of oxidized cotton yarns was analyzed by lost in tensile strength, elongation, work of rupture, CIE whiteness and CIELab coordinates.

Oxidized yarns exhibited slightly lower tensile strength, work of rupture and  $a^*$  and  $b^*$  values and higher CIE whiteness compared to unoxidized.

Key words: non-selective oxidation, cotton yarns, structural properties, carboxyl groups, degradation

T-8

## ANTIMICROBIAL ACTIVITY OF ECO-FRIENDLY DYED COTTON BY *CURCUMA LONGA L.* EXTRACT

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

Antimicrobial finishes of textile materials have become necessary for enhancing apparel performance along with meeting consumer - led future demands. Many commercial products are currently available on the market with the range of antimicrobial properties for textile industry. Majority of such products are synthetic based and may not be environment friendly. Natural dyes present in plants are less harmful on humans and environment so they play an important role as an alternative source to synthetic dyes. Curcumin (natural yellow pigment), the major pigment in turmeric rhizome extracts (*Curcuma Longa L.*) is widely used in the food industry as a condiment. Numerous reports suggest that curcumin has wide spectrum of biological and pharmacological activities including antioxidant, antibacterial, antifungal, antiviral, antitumor, anti-inflammatory, anti-coagulant activities.

Enzymatic scoured cotton knits with alkaline and acid pectinases were dyed with *Curcuma Longa L.* extract in combination with several mordant.

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

The antimicrobial efficiencies of dyed knitted goods with *Curcuma Longa L.* extract depends on the type of pretreatment as well as used mordant.

Key words: cotton, antimicrobial activity, *Curcuma longa L.*, enzymes.

**T-9**

**REVIEW OF MACHINE NEEDLES FOR THE SEWING PROCESS OF  
TECHNICAL TEXTILES AND LEATHER PRODUCTS**

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Machine needle is one of the main elements of the mechanisms involved in the formation of stitches. In order to avoid side effects, great attention is devoted in choosing the right sewing needle. Possible side effects often occur in the sewing process of technical textiles and leather products. Today, technical textile is increasingly present in the world. Its application is reflected as automotive textiles, home textile, medical textiles, protective and smart textiles, industrial textile, agrotech etc. These textiles with specific structures have so strong penetration forces that often lead to needle deflection. In order to prevent these problems, the world famous manufactures, such as company Groz-Beckert and Schmetz, develop new technology that lead to the stability of the needle. The paper gives an overview of launched products by these companies for sewing of heavy technical textiles and leather products. The achieved results are reflected in the reduction of skipped stitches, materials damage, point needle damage, breaking of thread and needle breaking.

Key words: sewing needle, technical textiles, leather, Groz-Beckert, Schmetz

## T-10

### **SEWING MACHINE STITCH FORMING PARAMETERS: UNFLUENCE OF SPEED AND FABRIC STRUCTURE VARIATIONS**

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Achieving high quality garments, besides incorporating high performance materials, requires providing quality in all stages of garment production. It is well known, that the process of garment construction is the most critical process regarding garment quality. In this respect, improving performance and flexibility of modern industrial sewing machines to adjust to various types of materials and shorten set-up times is of particular importance for achieving high-quality sewing operation.

For this investigation, the lockstitch industrial sewing machine, stitch type 301, was equipped with sensors for monitoring needle thread tension; thread consumption and presser foot displacement. The information about the behavior of the sewing cycle parameters were collected and stored on a pc and analyzed using specially developed program. Program enables graphical presentation of the thread tension and foot displacement variation during sewing cycle, as well as thread consumption.

A range of woven fabrics for men’s tailored clothing having variations in structure, were sewn using two sewing speeds. The influence of sewing speed and fabric structure variation on thread tension, thread consumption and presser foot displacement have been analyzed. The samples were tested in warp and weft directions. The results confirm the influence of the fabric structure and sewing speed on sewing process parameters.

*Keywords:* stitch forming parameters, sewing, clothing

T-11

## **ADSORPTION OF DIRECT DYES ON COTTON WITHOUT ANY ADDITION OF AUXILIARY AGENTS**

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Direct dyes are aromatic nitrogen compounds that dissolve in water due to existing sulphuric groups or other hydrophilic groups - carboxyl and hydroxyl. They are usually used for dyeing cellulose materials (cotton, viscose...) in the presence of electrolytes and wetting agents. Starting from the chemical frame of direct dyes, there are the carriers of free electrolyte pair groups that behave as electron donors, and carriers of hydrogen atom group - electron acceptor. Compounds that have any of previously stated groups are capable to connect at cellulose by creating hydrogen connection between hydrogen from hydroxyl cellulose group and free electron pair group from dye and/or between oxygen of hydroxyl cellulose group and hydrogen atoms from the dye. On the other hand, fibre structure shows that surfaces of structural elements are important for adsorption – fibrils, micro fibrils and secondary wall segments.

This paper aims to show dye adsorption ability for fibre in pure water environment using only three components (water, textile, dye) as precondition for appliance of various additives, which can improve adsorption of fibres dyeing in a sense of higher dye usage from solution. This is also due to dyes that are more or less sensitive on additives (electrolyte, surfactant) but due to more important fact that technical dyes are not chemically pure but they contain certain amount of salt, which improves more or less dye exhaustion from bath, in relation to dye nature and bath relation. According to this, if the dye exhaustion is higher, the less dyed wastewater is gained and it is less harmful for environment. In relation to this, it is necessary to decrease the amount of usual additives (or propose alternative, ecologically acceptable ones) since the large amount of salt or active surface substances, along the dye itself, disturb ecosystem, especially the water world.

Based on gained experimental results, the following things can be concluded: longer contact time means larger dye amount on the yarn; dye concentration in solution decreases during the adsorption process; continuity of used dye amount growth with adsorbent mass is noticeable; data gained from Langmuir equation show that the model does not provide enough precise description of experimental data; data gained from Freundlich equation show that the model provides precise description of experimental data.

Keywords: adsorption, cotton, direct dye, dyeing, Freundlich isotherm, Langmuir isotherm.

**MISCELLANEOUS (MISC)**

## MISC-1

### NATIONAL STANDARD FOR MASS

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Bureau of Metrology (BoM) is a National metrology institution of the Republic of Macedonia, which operates within the Ministry of Economy. The main objective of BoM, as specialized body is establishing the National standards of International SI-units, for providing traceability of the measurements in the country and with the world. The National metrology infrastructure must rely on global metrological infrastructure and world-wide achievements in fundamental metrology, for practically definition, realization and development of International standards of measurement units required for the provision of International unit of measure.

National calibration laboratories of BoM provided traceability of the measurement results of the measuring instruments to certain references, usually National or International standards, through the unbroken chain of comparisons. Traceability of the standards is maintained by their regular calibration in National metrological institutes (NMI), directly traceable to International measurement standards.

Mass calibration laboratory is a part of laboratory centre from sector for calibration and development at BoM. The primary goal of the mass calibration laboratory is to develop and maintain the National standard for mass through comparison with other metrological institutes, which are traceable to BIPM – International Bureau for Weights and Measures (Paris, France).

In the procedure for recognition of the National standard for mass there was necessary to meet all conditions for its realization, calibration, successful international intercomparisons as well as its storage and maintenance. The laboratory procedures include uncertainty determination, because many variables have influence during the calibration process.

Because traditionally and historically, the development of metrology began with mass measurements, in accordance with the anticipated development of Macedonian National metrological infrastructure, the first recognition of national standards begin with mass standard.

Key words: national standard, metrological infrastructure, calibration, uncertainty, traceability

## MISC-2

### **BIBLIOMETRIC ANALYSIS OF THE SCIENTIFIC ACHIEVEMENTS OF THE INSTITUTE OF CHEMISTRY IN SKOPJE, MACEDONIA**

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The Institute of Chemistry which is part of the Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University in Skopje is responsible for about 30% of all publications presented in international journals from Macedonian researchers. The research presented in this work was performed in order to get in depth insight into the achievements of the Institute as a whole, the achievements of its members and for exploration the new developments in the existing research groups. Beside this, using different data exploratory algorithms we explored the changes of the research trends through time in order to find which disciplines are popular at the moment, and which disciplines were popular in the past.

The bibliometric data analysis was performed using data collected from Web of Science. The data analysis was performed using tools such as self-organizing maps, graph theory and principal component analysis.

**Keywords:** bibliometry, self-organizing maps, graph theory, principal component analysis, exploratory data analysis.

### **MISC-3**

## **ASSESSING QUALITY OF LUBRICANTS MARKETED IN REPUBLIC OF KOSOVO**

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This work comprises the first efforts for analyzing, assessing and systemizing almost all kinds of imported oils in Republic of Kosovo. Although the attention and emphasis were given to lubricant oils, also transmission oils, hydraulic oils and those for transformers were analyzed. In the last year a remarkable increase in the number of vehicles is detected for both kinds, those that use gas-oil as well as those that use gasoline. This brings up greater consumption for both, the fuels and the lubricating oils that they use, as well as the necessity of controlling their quality, keeping in mind that the sources of our fuels' market supply are diverse.

Monitoring of the quality of lubricating oils traded in our country would help:

- First, in assessing the general characteristics of oils compared to European Standards.
- Second, in compiling and approving our Standards for lubricating oils.

The control of hydrocarbons in the territory of Kosovo is regulated by Law no. 2004/5 "On trade and diesel fuel" and under Administrative Nr.2008/21. In the material, given in form of bars, are analytical and detailed parameters for analyzed lubricating oils samples traded on the Kosovo market since 2008 and their distribution, based on parameters provided by Administrative and International Standards. According to that, the number of samples that are not meeting the standards were determined. Samples were analyzed at the Laboratory "Derivati" Eat Jankovic INKOS Institute, Kastriot-Kosovo. Physico-chemical analyses were made on 172 samples.

Key words: hydrocarbons, lubricating oil, the international standard

## MISC-4

# INTEGRAL MODEL FOR ROLES DISTRIBUTION WITHIN A WORKING TEAM

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Long-term and short-term efficiency and effectiveness depend on an optimal Roles distribution within a working team. Therefore, having a model which enables such corresponding distribution is of a high interest to any quality manager.

Two main concepts, the Roles concept of Adizes and Working styles concept of Kahler, are involved to create an integral model in this article with an original approach to the Roles distribution in any working team. The greatest advantage of this model is that it is predictive instead of experiential: it makes it possible to make a corresponding Roles distribution in advance within the team, without previously monitoring the activities of the potential team members. A discussion to the relation between the possible outcomes and the level of prediction is given.

Key words: integral model, Roles distribution, teamwork.

## MISC-5

# AN APPLICATION OF THE INTEGRAL MODEL FOR ROLES DISTRIBUTION FOR CREATING A MANAGING TEAM INTO A CERTAIN ORGANIZATION

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The creation of the integral model enables corresponding Roles distribution within a working team. This model is important because it helps improve the teamwork by making it effective and efficient into an original and elegant way. It may be particularly valuable to managers or company consultants who may propose this model at any time a team is being created, or if already created, to apply the model to team members for corresponding team activities distribution. This model may be also valuable to any team job interviewers, since it locates the job candidates within those who meet the main criteria (education, experience, skills, etc.) who are functionally the most optimal.

In this article an application of the integral model in an organization is presented. The application is rather simple and is very informative of the working behavior style of those to whom it is applied. A managing team in the organization is proposed.

Keywords: integral model application, Roles distribution, teamwork, managing team.

## MISC-6

### **A STUDY ON THE DEVELOPMENT OF THE KEY PERFORMANCE INDICATORS FOR A GARMENT COMPANY**

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The main goal of the paper is to present and discuss the way of establishing the Key Performance Indicators for measuring the company performance and productivity. The KPI-s methodology is like a health check-up for the company that helps to diagnose the actions to be undertaken in order to make improvements where it is necessary. Key Performance Indicators usually are considered on long-term basis.

For this study, 15 indicators for performance measurement for the garment production companies are explained, recommended and calculated to analyze and improve the general productivity of the company.

Keywords: Key Performance Indicators, improvement of productivity, performance measurement, effective hours of production.

## MISC-7

### IGNITION QUALITY OF DIESEL FUELS BY THE CETANE METHOD

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The cetane method provides means of determining the compression-ignition characteristics of diesel fuels. The cetane rating is a measure of an important combustion characteristic of a fuel in a compression ignition (diesel) engine.

A long ignition delay (low cetane) in a diesel engine will result in rapid pressure rise that can cause undesirable audible knock, high stresses and severe engine vibration. Also, difficult starting in cold weather, misfiring and excessive white smoke often result from too low cetane values. The official cetane rating is determined in a special engine defined by ASTM D613 and EN ISO 5165, Standard Test Methods for Cetane Number of Diesel Fuel Oil.

OKTA Refinery has apparatus for determination of the cetane number. It consists of a single cylinder engine of continuously variable compression ratio, with suitable loading and accessory equipment and instruments, mounted on a stationary base. OKTA Laboratory's experiences, by solving many problems (expected and unexpected), and this study is at the base of the results of our investigation.

Keyword: refinery , diesel engine , cetane number

## MISC-8

### DEFINING FACTORS OF EMPLOYEE MOTIVATION AND DEMOTIVATION: CASE STUDY IN MILL-BAKING INDUSTRY

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Quality assurance has to be one of the priority goals for every company. The effectiveness and efficiency of the quality assurance system is directly affected by the employee's dedication to this organizational goal. Therefore, the management has to be deeply engaged in increasing employee motivation.

In this study a new designed questionnaire for evaluation of job satisfaction was used. The questionnaire contains primary questions and sub-questions, where there was a need for additional clarification. The primary questions in the part of motivation include the factors: recognition, work itself, responsibility, possibility of growth, achievement and advancement. The primary questions in the part of demotivation include the factors: salary, working conditions, company policy and interpersonal relations with supervisors, subordinates and peers. The obtained responses were analyzed with descriptive statistic and xi-square test as a verification of objectivity of the obtained results by confirming the correlation of the grades distribution on the questions that are naturally connected. The analysis provides directions of management engagement and decreases the subjectivity in the selection of management practices.

The results showed that the general grade of employee's satisfaction in the analyzed company is **relative satisfaction**. In order to increase the employee's dedication to quality assurance, the management has to pay special attention to salary, perception of the ration of the employee's salary with the salary of their peers from the same and different organizational level, increased participation of the employees in the decision making process, designing rewarding system that will include the expected rewards for the work done.

Key words: quality assurance, work motivation, questionnaire, management, xi-square test

## MISC-9

### CRITERIA FOR ASSESSING THE SUCCESS OF NEW MANAGERS

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The rapid and frequent fluctuation of managers within an organization may have a negative impact on the performance of the organization itself. Therefore, the assessment of the success of the potential manager is highly important. This assessment also saves the energy of the organization in terms of investing in the development, progress and induction of the manager. In addition, the presumption that the level of success of the potential manager can be assessed and improved is important; thus the compatibility of the potential manager to the standards, objectives and mission of the respective organization can be influenced.

The authors conducted a research with experienced top managers, thus setting the standards considered as criteria for assessing the success of new managers. A discussion has been given and recommendation has been proposed for further comparison of the directions and benchmarks for success provided by the experienced managers, to the results that can be obtained by using proven methodologies and surveys with the new managers.

Keywords: manager, success criteria, teamwork

## MISC-10

# APPLICATION OF STATISTICAL METHODS FOR IMPROVEMENT OF THE RUSK PRODUCTION PROCESS

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The application of statistical methods in the production process is suitable and important for determination of the stability process, as well as in the improving quality and reducing of the costs and losses. The main goal in the production processes is to produce products on the instant in order to eliminate the costs linked with quality control, so number of nonconformity products is decreasing.

The possibility for application of the statistical methods in the production process of rusk designated as „dark village rusk“ was investigated in this work. The moisture quantity more than 2% was the main critical control point for rusk production. The scattering diagram, correlation and regression analysis, as well as statistical control cards were used in determination on the dependence between the moisture quantity and broken pieces of the rusk.

The quantity of cracked and broken rusk pieces by increasing of the moisture quantity increased. From the applied statistical control cards (p-cards) and obtained results for upper (5.57%) and lower (0.52%) limit for the percentage quantity of cracked and broken rusk pieces instability of the process was determined. The over baked rusk pieces were with a bitter taste. This imposed the requirement for selection of rusk pieces produced in the critical period, followed by its repackaging. In the organization of the production process of the rusk, it was necessary to adjust all the possibilities for optimum exploitation of machinery and raw materials, as well as to determine the most optimal conditions for the most rationally exploiting workforce, time and space. The overall efficiency of the production process of the rusk and therefore the company as a whole, by application of the statistical methods were increased.

Key words: rusk, correlation, regression, control cards

## MISC-11

# EVOLUTION AND PREVENTION OF WEAPONS FOR MASS DESTRUCTION

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The main theme in this paper is the evolutionary period of development of the unconventional weapons for mass destruction and preventive measures of international actors, particularly countries that are hegemonic especially in having a nuclear arsenal, represent with rocket missiles for medium and long range distance in the world (USA and Russia).

Evolutionary development of NHB weapons particularly is in the time of the First World War when getting combat and operational advantage over the opponent is increasingly used various types of colored chemical poisons (sulfur and nitrogen mustard gas, blood battle toxins, etc.).

The development of nuclear weapons is especially noticeable at the end of the Second World War. When the USA immediately after the war begins to develop and strengthen its nuclear arsenal, which after were followed by other international actors.

In this paper we summarize the evolutionary process of the nuclear arsenal in the period after the Second World War until today, which will particularly address the preventive measures and mechanisms of anti proliferative, operational and tactical destruction of this kind of weapons and measures to store nuclear waste as a part of critical infrastructure, defined in the new strategic concept of NATO adopted in Strasbourg and Cologne in 2009 year.

Finally through the methods of comparison and analysis, we will give the future prospects of the world if preventive measures for protection against the weapons of mass destruction will be didn't taken.

Key words: Evolution, weapons of mass destruction, prevention, New strategic concept of NATO, perspectives.

## MISC-12

### **BASIC ASPECTS OF PROJECT APPROACH OF THE IMPLEMENTATION OF THE INTERNATIONAL STANDARD ISO 22000:2005**

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International standard ISO 22000:2005 specifies requirements for the implementation of food safety management system. This standard is applicable to all organizations, regardless of their size, which are engaged in any aspect of the food chain. On the other hand, the project approach of the implementation of this standard is essential for the organization itself. The project approach to implementation of this standard has to cover all aspects including: planning, organizing, monitoring and control in a continuous process of managing food safety, using of appropriate knowledge, skills, tools and the techniques. The project approach to implementation of ISO 22000:2005 can be seen at the request of the organization to establish, document, implement and maintain an effective system of food safety, with special focus on promotion in accordance with principle of PDCA cycle. The basic elements of the implementation of the international standard must analyze three main aspects of management: time, resources and costs. This paper is based on several case studies of implementation of food safety management system ISO 22000:2005.

Keywords: Project, standard, food safety.

## MISC-13

### OBSERVATION AND IDENTIFICATION OF ANTHROPOGENIC IMPACT ON DRINKING WATER QUALITY IN TIRANA URBAN AREA

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In Tirana, Albanian capital city was found polluted drinking water caused by different and various sources brought about by demographic movements and excessive land use. This work attempted to carry out and evaluate the experimental measurements of water quality conducted in the most populated urban areas in metropolitan city of Tirana, Albania.

The analyzed samples has been collected regularly every month during the whole 2011 year, until June 2012 and sampling sites were located in the main thirty one road arteries. The physical-chemical parameters analyzed during seasonal variations include: water temperature, salinity, conductivity, pH, organic material, total dissolved solids (TDS), and chemical ions such as: chloride (Cl<sup>-</sup>), Ammonia (NH<sup>4+</sup>), and nitrites NO<sup>2-</sup>.

We observed that the quality of drinking water is influenced mostly by organic and nutrients (anthropogenic) pollution from domestic wastewater. Also, a contribution comes from the large number of constructions areas which interfere in the main pipelines of water sources. Due to heavy rains, high values of Ammonia (NH<sup>4+</sup>), and nitrites NO<sup>2-</sup> were measured in September, October and November in the areas with higher population number and road traffic circulation.

**Keywords:** water analysis, drinking water, pollution, chemical composition

**MISC-14****POSSIBILITIES FOR OBTAINING OF CONTEMPORARY EUROPEAN  
GASOLINE BY ALTERNATIVE METHOD**Yordanka Tasheva<sup>1</sup>, Petko Petkov<sup>2</sup>

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A modern refinery is a highly integrated industrial plant, the main task of which is to efficiently produce high yields of valuable products from a crude oil feed of variable composition. Employing different physical and chemical processes such as distillation, extraction, reforming, hydrogenation, cracking and blending the refinery converts crude oil to higher value products. The main products are liquid petroleum gas, gasoline, jet and diesel fuels, wax, lubricants, bitumen and petrochemicals. Energy and hydrogen for internal and external use are also produced in a refinery. Currently, refineries meet changing societal needs concerning product specifications and quality by upgrading existing technologies and continuously developing advanced technologies [1].

Environmental restrictions regarding the quality of transportation fuels produced and the emissions from the refinery itself are currently the most important issues, as well as the most costly to meet. The primary goal of the recently proposed regulations (by the Directive of the European Parliament [2] and the Environmental Protection Agency (EPA) Clean Air Act (Tier 2) [3]) is to reduce the sulfur content of transportation fuels. The CO<sub>2</sub> emitted by the refinery into the atmosphere is limited by the Kyoto protocol [4]. According to various estimation models, \$10–15 billions in the European refinery industry and up to \$16 billion in US and Canadian refineries will be invested in direct response to the new environmental clean-fuel legislation [5,6]. Gasoline, diesel and non-transportation fuels account for 75–80% of the total refinery products. Most of the desulfurization processes are therefore dealing with the streams forming these end products. Sulfur present in the fuels leads to SO<sub>x</sub> air pollution generated by vehicle engines. In order to minimize the negative health and environmental effects of automotive exhaust emissions the sulfur level in motor fuels is minimized. New sulfur limits of 10 ppm for gasoline and diesel marketed in the European community and the USA will be introduced starting from January 1, 2007 [10]. Bulgaria has even passed legislation limiting the sulfur in diesel and gasoline to 10 ppm as of January 2010 [10]. In fact, zero-emission and, as a consequence, zero levels of S are called for worldwide in coming 5–10 years. Such ultra low-sulfur fuels requirements have consequences for the refinery. Efficiency of the desulfurization technologies becomes a key point. Conventional hydrodesulfurization (HDS) processes cannot currently produce such zero sulfur level fuels, while maintaining other fuel requirements such as oxygen content, vapor pressure, benzene content, overall aromatics content, boiling range and olefin content for gasoline, and cetane number, density, polynuclear aromatics content, and distillation 95% point for diesel fuel [11].

Keywords: advanced technologies, solvent, petroleum products

## MISC-15

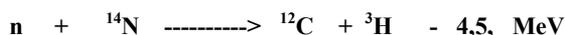
## APPLICATION OF TRITIUM DISTRIBUTION IN DETERMINATION THE KINEMATIC AGE OF GROUND WATER

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Water supplies especially in the urban areas represent one of the greatest present problem all over the world. Tritium (<sup>3</sup>H or T) as a natural radioactive isotope of the Hydrogen with a half-life time (T<sub>1/2</sub>) of 12,26 years, with the smallest mass and the highest different in masses of the isotopes that belong to the same element, starting from its discovery rose a great interest firstly among the physicists working on the theory of radioactive decay and later, up to present days, among the hydrogeologists who use it as a natural tracer of water into its hydrological cycle. This tracer has been accepted as an efficient tool in groundwater hydrology in particular due to the fact, that after its formation into the upper atmosphere according to the following equation,



oxydise to water, giving HTO, for later with the precipitations to reach the ground and ground water. In the simplest way (Piston flow model), precipitations after its infiltration into the ground, the concentration of the Tritium start to decrease following the law of radioactive decay, resulting in the possibility to determine the age of the observed ground water.

In this paper two case studies are discussed, determining the volume of the Aquifers feeding the St Naum Spring (Ohrid) and Rasche Spring (Skopje) as well as their MRT. According to the geological conditions and hydrogeological characteristics of the Ohrid-Prespa Region, observed tritium concentration into the local precipitations, Prespa Lake water and spring water of St Naum, a one cell model of two mixing components ( Precipitations over Galicica Mountain and infiltrated through Galicica Mountain, Prespa Lake Waters) has been proposed. By using the above mentioned model, Delphi programming language and the following recursive equation,

$$S_{t-1} = ( S_0 + GFO * GCO - GFI * GCI ),$$

the volume of the reservoir under the Galicica Mountain that recharge the St Naum Spring as well as the mean residence time of the ground water of have been determined and the respective values of cca  $3,1 \times 10^9 \text{ m}^3$  and 5 years were received.

Almost the same methodology (one cell mixing model of two components) has been applied during the researches performed on the Rasche Spring, as well. Having no evaporation effect like it was in the case of Prespa Lake, beside the Ground water component (deep artesian water in Dolen Polog) to the component of precipitation over the Zeden Masiff, Vardar River contribution has been added, as their tritium concentration values have followed these observed in Precipitation. In this case, for MRT we have received a value of cca 27 years.

Key words: environmental isotopes distribution, tritium simulations, ground water kinematic age determination

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