



Croatian Society of Chemical Engineers
Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek
European Federation of Food Science and Technology
European Association for Chemical and Molecular Sciences
European Hygienic Engineering & Design Group

International Scientific and Professional Conference

15th Ružička days

“TODAY SCIENCE – TOMMOROW INDUSTRY”



11th and 12th September 2014
Vukovar, Croatia

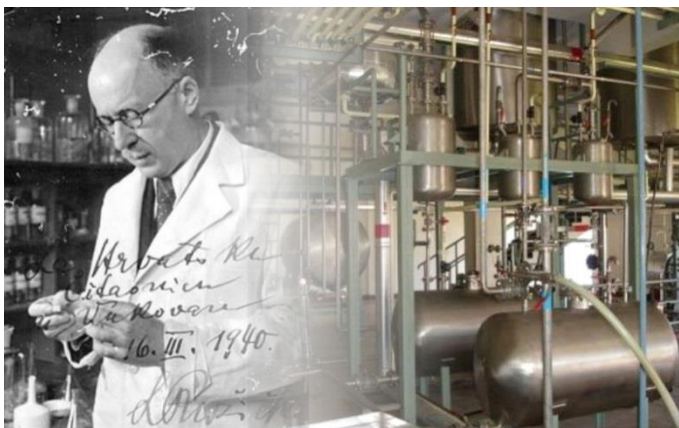
BOOK OF ABSTRACTS

Hrvatsko društvo kemijskih inženjera i tehnologa
Prehrambeno-tehnološki fakultet Sveučilišta Josipa Jurja Strossmayera u Osijeku
European Federation of Food Science and Technology
European Association for Chemical and Molecular Sciences
European Hygienic Engineering & Design Group

međunarodni znanstveno-stručni skup

XV. Ružičkini dani

“DANAS ZNANOST – SUTRA INDUSTRIJA”



**11. i 12. rujna 2014.
Vukovar, Hrvatska**

KNJIGA SAŽETAKA

Osijek, 2014.

KNJIGA SAŽETAKA XV. Ružičkini dani
DANAS ZNANOST - SUTRA INDUSTRIJA

BOOK OF ABSTRACTS 15th Ružička days
TODAY SCIENCE – TOMORROW INDUSTRY

Izdavači Prehrambeno-tehnološki fakultet Osijek
Hrvatsko društvo kemijskih inženjera i tehnologa (HDKI)
Published by Faculty of Food Technology Osijek
Croatian Society of Chemical Engineers

Glavni urednik
Chief Editor Drago Šubarić

Izvršne urednice Mirela Planinić
Executive Editors Đurđica Ačkar

Tehničke urednice Ivana Pavleković
Technical Editors Đurđica Ačkar

Lektor
Proofreader Antonija Šarić

Dizajn naslovnice
Cover sheet design Ivana Pavleković

Tisak i uvez
Printing and Binding Grafika d.o.o., Osijek, Hrvatska

Naklada
Number of Copies 250

Znanstveno-organizacijski odbor
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Skender, Nenad Trinajstić, Željko Turkalj, Ivan Vrdoljak

ISBN (PTF): 978-953-7005-34-4
ISBN (HDKI): 978-953-6894-52-9

CIP zapis dostupan u računalnom katalogu
Gradske i sveučilišne knjižnice Osijek pod brojem 131120016
A CIP catalogue record for this publication is available from the
City and University Library Osijek under 131120016

Pokrovitelj:

Hrvatska akademija znanosti i
umjetnosti
Razred za matematičke,
fizičke i kemijske znanosti

Under the Auspice of:

*Croatian Academy of Sciences and
Arts
Department of Mathematical,
Physical and Chemical Sciences*

***Uz potporu:***

Ministarstvo znanosti,
obrazovanja i sporta
Republike Hrvatske

Supported by:

*Ministry of Science, Education and
Sports of the Republic of Croatia*



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Hrvatske

Croatian Academy of Engineering



Sveučilište Josipa Jurja
Strossmayera u Osijeku

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Vukovarsko-srijemska
županija

Vukovar-Srijem County



Grad Vukovar

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 (crtice za povijest o 14 znanstveno-stručnih skupova „Ružičkini dani“
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4. Susret mladih kemičara

4th Meeting of young chemists

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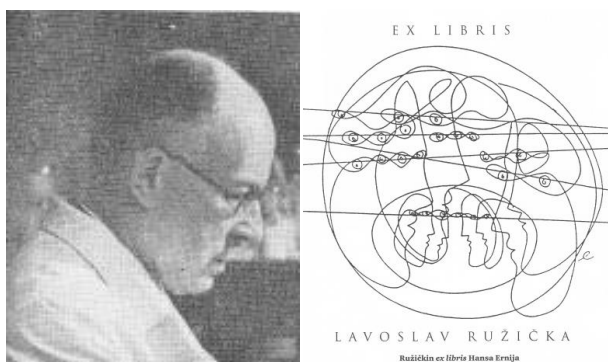
Pozvano predavanje
Invited lecture

**Nobelovac Leopold (Lavoslav) Ružička, rođen 1887. godine u Vukovaru
(crtice za povijest o 14 znanstveno-stručnih skupova „Ružičkini dani“
/1978-2012/, o Vukovaru i o Vukovarcima; ex libris¹)**

**Nobel Prize winner Leopold (Lavoslav) Ružička, born in 1887 in Vukovar
(historical vignettes of 14 scientific-professional conferences "Ružička days"
/ 1978-2012 /, about Vukovar and the people of Vukovar; ex libris²)**

Ivan Hubalek

Miroslava Krleže 24, HR-31207 Tenja, Croatia (retired, a former employee of "Borovo" Plc Vukovar)



Leopold (Lavoslav) Ružička, Nobel Prize winner for chemistry (1939), born in Vukovar on 13th September, 1887, died on 26th September 1976 in Malmern (Switzerland), was surely the most famous citizen of the city of Vukovar.

Many have spoken and written about this great chemist man and they all pointed out that his greatest love was the love for his work, his most distinctive virtue - modesty. We are familiar with his sayings: *Many eyes see better than two eyes* and *A single professor is better than the sum of his associates* which has served Hans Ernie to develop Ružička Ex Libris. He is also known for his humanitarian work in the Second World War.

¹ex libris (lat.; na hrvatskom jeziku glasi „iz knjiga“, „između knjiga“, a znači zapravo „iz knjižnice“)

²ex libris (lat.; translated into Croatian language means "from the books", "between the books" and actually means "from the library")

Pozvano predavanje / Invited lecture

In his humility, he talked little about himself, his family, his origin.

This work will not cultivate the scientific contribution of Nobel Prize winner Ružička to the world science, but it will remind us of what is written (in books, journals, newspapers): about his origin and relation to Vukovar, while he was alive. We will remind ourselves of what he did in Vukovar so that he never gets forgotten. A brief description of the city of Vukovar will be introduced.

He lived in Vukovar for only 4 years and he could not remember it but Vukovar remembered Ružička and was proud of him. This was demonstrated during the meeting between Ružička and Vukovar citizens in March 1940, during the promotion of Lavoslav Ružička for the honorary doctor of the Croatian University in Zagreb, and "the Nobel Prize award". Nikola Pšenica, born in Vukovar, wrote about this (then president of the Croatian Chemical Society) *Doctor Lavoslav Ružička, meritorious son of the town of Vukovar, who celebrated the name of his birth Place around the whole world*. From the writings we learn of Vukovar donors, about the "Foundation of the late Šandor Najpar and widow Mary from Vukovar", who donated 100.000 dinars to the University during the promotion of Lavoslav Ružička for the honorary doctor of the Croatian University in Zagreb.

Ružička was in Vukovar in 1963 and again in 1965. His wish to visit his hometown once more was not fulfilled.

He donated to his hometown a part of his legacy, which was the backbone of the Memorial Museum Ružička, opened on 9th December 1977 in his birth house. The birth house and museum were severely demolished during the war in Croatia (in 1991). Today the house is renovated and the 15th international scientific-professional conference "Ružička days", which has taken place since 1978 will be held there this year as well.

The longevity and continuity of "Ružička days" conference in Vukovar gives us the opportunity to get acquainted with the latest scientific and technical achievements, but also to remind with this lecture of the Nobel Prize winner Leopold (Lavoslav) Ružička and to introduce Vukovar, a European city on the Danube.

Plenarna predavanja
Plenary lectures

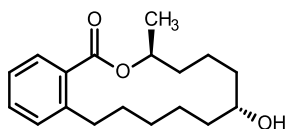
Od znanosti do industrije – i natrag

From science to industry – and back

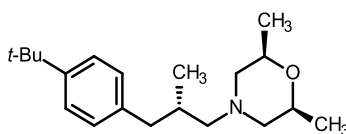
Vitomir Šunjić

Croatian Academy of Science and Arts, Zrinski trg 11, HR-10000 Zagreb, Croatia

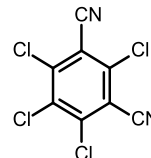
Biological activity of organic compounds, either from the natural sources or from the laboratory, represents the base for human therapy, veterinary application, in agro-complex (insecticides, fungicides, herbicides), or in food industry. During my main research activity on the synthesis, structural and biological studies of the compounds with potential, or confirmed, activity in human therapy, my team occasionally participated in the projects related to some of the above mentioned fields. In this presentation research, synthesis, biocatalysis, structural and conformational analysis and biological properties related to one anabolic applied in the meat production (α -Zearanol), and two fungicides ((S)-Fenpropimorph and Chlorothalonil) will be explained.



α -Zearanol



(S)-Fenpropimorph



Chlorothalonil

Research activities on these projects are completed either in the industry or in collaboration with an industrial partner. These projects, however, regularly resulted in new knowledge that suggested new academic research activities; on the effect of the group remote from the stereogenic (chiral) center in the substrate on enantioselectivity of the lipase catalyzed processes, proposal of the new model for the effect of absolute conformation on stereoselectivity of the enzyme catalyzed reactions and development of new chiral stationary phases (CSPs) for the separation of enantiomers from the racemic mixture. This last example will show how new knowledge in one scientific field creates new ideas (and commercial projects!) in another, seemingly unrelated field.

Razvoj i komercijalizacija novih aseptičkih tehnologija za preradu hrane i biomaterijala: Sterilizacija primjenom mikrovalova pod kontinuiranim protokom i integrirani sistemi za praćenje toka krutih sastojaka

Development and commercialization of new aseptic technologies for processing of foods and biomaterials: Continuous flow microwave sterilization and integrated systems for particle flow monitoring

Josip Šimunović

Department of Food, Bioprocessing and Nutrition Sciences, North Carolina State University, Raleigh, NC, USA

After decades of research and development, several emerging technologies have been recently commercialized for industrial preservation of foods and biomaterials. These include ultra-high pressure processing, pulsed electric fields and sterilization using volumetric technologies like ohmic, radio frequency and microwave heating. These technologies hold the potential to process and preserve products with better retention of sensory quality (color, flavor, texture) and thermo-sensitive nutrients. Additionally, aseptic processing and preservation of products, which have not been previously feasible, became possible, such as low acid products containing large particulate components like chunky soups. In order to introduce such products to consumer markets, these new processes (appropriate sterilization treatments) need to be validated in order to scientifically establish the safety of the final products and satisfy the requirements of regulatory agencies like FDA and USDA.

Two new aseptic processing technologies for foods and biomaterials have been recently developed by our team: continuous flow microwave sterilization, also known as microwave-assisted aseptic processing and integrated systems for particle flow monitoring and validation. This presentation will review the initial concepts, increments of development and implementation, sequential studies and expansion of capabilities and their eventual commercialization in United States and Europe, with examples of products produced through their implementation.

Trehaloza: multifunkcionalni šećer i njegove primjene

Trehalose: multifunctional sugar and its applications

Takanobu Higashiyama

NAGASE (EUROPA) GmbH/ Hayashibara, Immermannstr. 65c, 40210 Dusseldorf, Germany

Trehalose is a naturally occurring disaccharide that possesses various functional properties. This unique disaccharide is a non-reducing sugar that consists of two glucose molecules linked by an α, α -1,1 glucosidic bond. Its physical properties include non-participation in the Maillard reaction, high heat and acid/alkaline resistance, one of the highest glass transition temperatures of common saccharides and low hygroscopicity. Therefore, it is one of the most stable saccharides, and because of its stability trehalose has excellent compatibility with other ingredients.

Trehalose is known to be an important energy source in many organisms and can be found in a wide variety of organisms, such as fungi, insects and plants. In nature, trehalose protects organisms against various stresses, such as dryness, freezing and osmopressure. Anhydrobiotic organisms, such as the Resurrection Plant (*Rosa de Jericó*), are able to tolerate almost total dehydration owing to their ability to synthesize large quantities of trehalose inside the organism. Trehalose can stabilize biologic membranes and other macromolecules under extreme environmental stress. A high glass transition temperature allows trehalose to maintain a stable amorphous structure without recrystallization under a wide range of environmental conditions. The glass state enables trehalose to form a "cast" around biomaterial protecting the molecules by restricting their molecular mobility and subsequent chemical reactions.

Although these properties have been recognized for many years, trehalose was not produced on an industrial scale because of the cost of manufacture. In 1994, Hayashibara Co., Ltd., Okayama, Japan, developed a novel enzymatic process for the production of trehalose from starch. This dramatically reduced the cost to permit widespread application, including the food industry.

The unique properties make trehalose a novel multifunctional sugar that can be used for innovative applications in food products, such as bakery, snacks, confectionaries, beverages, meats and frozen foods, as well as vegetable and fruit categories. The use of trehalose can help maintain the natural quality of foods during manufacture, storage and distribution, which can turn into fresher products with longer shelf-life for the consumer.

Trehalose has been commonly consumed in the human diet for many years. It is a fully caloric sugar whose digestion and metabolism is similar to other disaccharides. Regulatory approval as a novel food was granted in Europe in 2001, and trehalose is now approved for use by almost all regulatory agencies throughout the world. Trehalose is also being used for various applications in the fields of cosmetics, health and beauty and pharmaceuticals.

[1] T. Higashiyama, *Pure and Applied Chemistry* 74 (7) (2002) 1263-1269.

[2] A.B. Richards, T. Higashiyama, Trehalose. In K. O'Donnell, & M. Kearsley, *Sweeteners and Sugar Alternatives in Food Technology*, 2nd Edition, 2012, (pp. 412-428).

**Izazovi u primjeni pozitronske emisijske tomografije:
od sinteze do ispitivanja na miševima**

**Challenges in positron emission tomography application:
from synthesis to testing on mice**

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Molecular imaging is an emerging technology that allows the visualization of interactions between molecular probes and biological targets. The interest in positron emission tomography (PET), as a sensitive, non-invasive molecular imaging technique, has steadily grown during the last three decades, and PET has currently been widely applied in the field of oncology, cardiology and neurology. Despite the recent development of novel PET imaging applications, the overall number of clinically-used molecular imaging probes is still small, when compared to the large number of disease-related biological targets that have been identified in the recent years. Thus, new PET probes are needed to fulfil the promise of molecular imaging, to assist in diagnosis of disease and therapy monitoring, and to support therapeutic drug development.

In an attempt to further explore the pyrimidine scaffold as putative starting point for development of novel PET tracers, we have identified a new series of C-6 and N-1 alkylated pyrimidines as PET probes [1-4]. The syntheses, ¹⁸F-labeling, biochemical and biological evaluations *in vitro* of PET tracer candidates were performed. The demonstration of monitoring efficiency of the best candidate *in vivo* using tumour-bearing mice will be also presented.

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Sadašnji trendovi u profiliranju aktivnosti i selektivnosti molekula s terapijskim djelovanjem

Current trends in activity and selectivity profiling of therapeutic molecules

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Drug discovery is a long process that starts with identification and validation of a new “druggable” target followed by testing many natural or synthetic compounds in assays relevant to the disease in question. A considerable portion of drug discovery process focuses on the target-specific assays, as well as those that assess off-target effects and cytotoxicity, which are all helpful in generating a broad profile of tested compounds reactivity. Carrying out numbers of studies prior to clinical trials such as improved *toxicity testing in vitro* and *in vivo*, establishing predictive translations models based on a thorough disease understanding and identifying biomarkers may help in the activity profiling of compounds with therapeutic potential. High affinity and selectivity are two of the most required properties of therapeutic molecules. Selectivity has been difficult to achieve, especially for targets that belong to large families of structurally and functionally related proteins. There are two ways by which selectivity can be improved during optimization: a chemical modification of the lead compound that improves the affinity towards the target to a higher extent than to off-target molecules, and a chemical modification that lowers the affinity of the lead compound towards off-target molecules. Maximal selectivity is achieved when both mechanisms can be combined synergistically. After high-throughput screening, hit compound identification, lead compound optimization, the drug discovery process ends with the launch of new active therapeutic molecules.

Usmena priopćenja
Oral presentations

Direktna potenciometrijska metoda za određivanje stresa kod ljudi

Direct potentiometric method for human stress determination

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Ptyalin is one of the principal salivary proteins. Ptyalin is a calcium-containing metalloenzyme and degrades starch by hydrolysing its linear α -1,4-glycosidic linkages, producing dextrans and ultimately maltose [1]. Since ptyalin secretion is regulated by the sympathetic nervous system which stimulates acinar cells of the salivary glands via β -adrenergic receptors, ptyalin activity varies under different conditions. There have been numerous reports on the impact of physical exercise on ptyalin activity [2]. All have found a significantly higher concentration of ptyalin during intense exercise in comparison to a control. Exercise is considered as a temporary stress activity.

There are several different assay methods available for determination of α -amylase activity. Different industries and laboratories tend to rely on different methods, including spectrophotometry, fluorometry, amperometry, electrophoresis, isoelectric focusing, chromatography and immunological methods [3-5]. Most of the methods are time-consuming and expensive (considering instrumentation, or chemicals). At present, the international standard measuring method of the human ptyalin activity is not assigned, and there is an obvious need to present and register one.

In this work, a direct potentiometric method for the determination of ptyalin activity in saliva was proposed. This analytical methodology is based on the direct potentiometric determination of free triiodide ion levels that are reduced due to the amount of remaining nonhydrolysed starch that forms a complex with triiodide [6]. A platinum redox electrode was used as a sensor to detect changes in triiodide concentration, which are directly correlated with ptyalin activity. The used instrumentation is low cost and easy to use, with high microfluidic automation potential.

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**Forenzički pristup analizi boja u spreju primjenom
svjetlosne mikroskopije i vibracijske spektroskopije**

**Forensic approach to analysis of spray paints by the use of
optical microscopy and vibrational spectroscopy**

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Forensic experts are often in a position to analyse spray paint samples (graffiti) that are, as offensive messages, mainly written on building facades. Since the layer of spray paint is usually thin and difficult to be separated from the substrate, it is necessary to apply the instrument techniques that do not require sample preparation prior to their analysis.

A total of ten black and blue spray paints with different hues were deposited on the clean glass slides as well as on the layer of white and yellow facade paint.

These model samples were *in situ* analysed using attenuated total reflection infrared spectroscopy (ATR-FTIR) and Raman micro spectroscopy, while the surfaces morphology were characterized by optical microscopy.

Binder compositions of all paints were successfully determined by IR, whereas Raman spectra obtained at laser wavelength of 785 and 532 nm provided the information about pigment contents.

In the IR and Raman spectra of the paint samples deposited on the facade paints no additional bands that would indicate the substrate influence were observed.

The research showed that non-destructive techniques used allow identification and differentiation of spray paint samples without previous preparation, as far as the thickness of the paint layer is sufficient to prevent the substrate influence.

Projektiranje laboratorijskog uređaja za ekstrakciju superkritičnim fluidima

Supercritical fluid extraction laboratory plant design

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A traditional solvent extraction method requires relatively large quantities of solvents, leaving toxic solvent residue and causing degradation of unsaturated compounds. Due to this fact there is an increasing demand for different extraction techniques which provide shortened extraction time, reduced organic solvent consumption, and decreased pollution. Supercritical Fluid Extraction (SFE) technique presents various advantages over traditional methods, such as the use of low temperatures, reduced energy consumption and high product quality due to the absence of solvent in extracts. In SFE process, environmentally friendly CO₂ is primarily used as an extracting agent.

The aim of this work was the design and development of a supercritical CO₂ extraction system used for laboratory measurements based on existing commercial systems. Alongside with the developed laboratory plant, an electronic system and PC application were developed for process control and future automation to achieve most accurate extraction parameters for production of quality extracts. The developed SFE system was examined in contrast with existing commercial systems to compare the efficiency of the system.

Uvećanje sušionika s fluidiziranim slojem

Scale-up of fluid bed dryer

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Scale-up in chemical engineering is usually based on laboratory scale experiments performed with at least two or three pieces of geometrically similar equipment and derivation of scale-up rules. Generally speaking, derivation of scale-up rules based on dimensional analysis cannot be applied on the drying process since a large number of parameters influence the drying kinetics. Taking into account only the simultaneous transfer of momentum, heat and mass, it is quite obvious how complex the drying process is. In fluid bed drying the situation is even more complex due to the chaotic motion of particles in the stream of hot air resulting in non-uniform hydrodynamic conditions. Besides that, the flow regime is greatly influenced by the dryer size so it is very hard to predict the drying kinetics in a larger scale dryer.

In order to define the scale-up rules for a fluid bed dryer, spherical particles of $\text{Al}_2\text{O}_3\text{-NiO-CaCO}_3$ catalyst were dried in two geometrically similar laboratory fluid bed dryers. Experiments were performed at different temperatures and flow rates of the drying air, for three bed heights. Minimum fluidization velocity was determined experimentally for both dryers. Based on the obtained results, it can be concluded that the size of the dryer influences the drying kinetics of spherical particles. The drying kinetics was approximated by the Page model. Evaluated parameters were correlated with the drying conditions and the size of dryer. Scale-up rules for minimum fluidization velocity and drying kinetic curve were defined.

**Djelomično pročišćavanje enzima NADH oksidaze
iz mikroorganizma *Lactococcus lactis* subsp. *cremoris***

**Partial purification of enzyme NADH oxidase
from *Lactococcus lactis* subsp. *cremoris***

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Upotreba NAD⁺/NADH-ovisnih oksidoreduktaza u biotehnologiji je od velikog značaja, ali im je primjena ograničena jer za svoje djelovanje zahtijevaju koenzime koji su skupi. Kako bi se uštedilo na koenzimu, razvijene su metode regeneracije koenzima (biološke, enzimatske, elektrokemijske, kemijske i fotokemijske). Jedna od jednostavnijih metoda je dodatak enzima za regeneraciju, npr. NADH oksidaze za regeneraciju koenzima NAD⁺-a. Prednost ovakvog načina regeneracije koenzima je u tome što NADH oksidaza katalizira ireverzibilnu reakciju kojom nastaje voda, a reaktant je kisik.

U ovom radu je mikroorganizam *Lactococcus lactis* subsp. *cremoris* izoliran iz parmezana *Parmigiano reggiano* (Galbani). Nakon uzgoja mikroorganizma u bioreaktoru, stanice bakterije razbijene su ultrazvukom u svrhu izolacije enzima NADH oksidaze, nakon čega su proteini taloženi isoljavanjem s 55 i 80% amonijevog sulfata te djelomično pročišćeni gel filtracijom (Sephadex G-50 i Sephadex G-100) i ionskom kromatografijom.

Izoliran i djelomično pročišćen enzim je testiran za regeneraciju koenzima NAD⁺ u sustavu oksidacije L-metionina katalizirane L-fenilalanin dehidrogenazom. Ravnoteža ove reakcije bez regeneracije koenzima je termodinamički izrazito nepovoljna. Uz NADH oksidazu je postignuta 100%-tna konverzija L-metionina u 2-okso-4-metiltiomaslačnu kiselinu uz znatno smanjenu potrošnju koenzima na temelju čega se može zaključiti da je regeneracija koenzima uspješno provedena, a ravnoteža reakcije pomaknuta u željenom smjeru.

Proizvodnja biodizela: esterifikacija suncokretovog ulja katalizirana lipazom

Biodiesel production: sunflower oil esterification catalyzed by lipase

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Biodiesel is a mixture of alkyl esters of fatty acids originated from a biological source. Due to its similarities with petroleum diesel, it can be used in diesel engines as an alternative fuel.

Currently, the industrial production of biodiesel e.g. transesterification is conducted chemically with alkaline catalysts. In this work, enzymatic synthesis of biodiesel was investigated. Enzymatic catalysis offers numerous advantages since it is performed under mild conditions, without additional energy consumption, with simple glycerol removal and without generation of chemical waste [1].

Transesterifications of edible sunflower oil catalysed by lipase from *Thermomyces lanuginosus* (Lipolase 100L) were conducted in laboratory batch and fed-batch reactors using methanol as alkyl donor. Experiments were conducted at three different temperatures ($T = 40, 50$ and $60\text{ }^{\circ}\text{C}$) and by two different mechanisms: one-step and four-step reactions. The four-step mechanism was carried out in order to avoid inactivation of the enzyme with methanol [2]. In the one-step experiment the molar ratio of oil to methanol was 1 : 3.4, while in the four-step experiment the molar ratio of oil to methanol at the beginning of the process was 1:1, after which methanol was fed into reaction mixture every 12 hours (molar ratio of oil to methanol was 1:0.8). All experiments were performed for four days using equal lipase initial concentration ($\gamma_E = 0.1\text{ mg/mL}$; S.A. = 100 000 U/mg). The highest conversion of fatty acids into corresponding esters of $X = 95\%$ was achieved for one-step reaction performed at $40\text{ }^{\circ}\text{C}$.

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Analiza „otisaka“ hrane metodom stabla odlučivanja

Decision tree analysis of foodprints

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Due to the application of modern instrumental methods for food analysis, based on IR, NIR, VIS, and MS spectroscopy and automation and robotics for sampling and pretreatment, large and complex sets of data associated with food physical, chemical and biological information are available. The advancement of experimental “high throughput” characterization needs to be followed with equally efficient, robust and validated algorithms for data analysis. Nowadays, with current experimental techniques modern software tools and extensive data bases with standardized reference records are available. However, the inference of important on-line information relevant for food production and product quality must be “in-house” developed for each specific product. Especially important is the integration of large data sets to a higher level of process knowledge in the form of input-output models applicable to dynamic aspects of process control. Such models are used for the detection of feed-stock and product adulteration, quality classification, early detection of process faults on production lines, product quality insurance, and optimal process control. For these various applications, the main common feature is synthesis by projection of multivariate information to low-dimensional latent variable spaces for extraction of the essential object -defined information. Various numerical and statistical methods have been developed and become routines in scientific literature, such as principal component analysis (PCA), principal component regression (PCR), partial least squares (PLS), artificial neural networks (ANN), K-means clustering, vector supported machines (VSM), and decision trees (DT). Decision trees are very simple models which are able to capture expert knowledge in the form of standardized procedures or steps, for example for quality insurance and adulteration proofing. In contrast to expert-designed decision trees, the supervised algorithm can be applied to “raw” experiments for modeling in classification and for quantitative structure-activity relations (QSAR). Examples for decision tree analysis on MS and NIR data applied to various Croatian products are given here, such as olive oil authentication, tangerines, wheat cultivars, and authentication of Adriatic island produced oils from *Lavandula* plants. The application of computer language R and availability of numerical, statistical and graphical tools is emphasized [1].

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Implementacija zahtjeva IFS-a u prehrambenoj industriji – izbor ili uvjet opstanka na tržištu

Implementation of IFS in food industry – option or condition of survival on the market

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The application of IFS requirements in companies is voluntary. Companies themselves make the decision on the need for the implementation of these requirements, depending on the evaluations which are in most cases based entirely on an assessment of market demand (customers). The implementation of the system is not a legal obligation and this results in the question of justification for the alignment process with this standard.

On the other hand, today's society, highly developed consumer awareness and increasing social and legal responsibility of food manufacturers place high demands on the hygiene and safety of products. The above is further extended to retailers who engage in selling their own brands and their names are at risk of being endangered. All this results in the fact that companies who want to do business with retail chains, export products and work with large customers today must implement IFS. The obligation to implement the standard has become a common condition for business cooperation, and survival in the market.

This paper presented the IFS requirements and the basic benefits of their implementation in companies. The implementation of IFS in a company improves the market position of the company but also provides better and "safer" product and facilitates access to new customers.

Bazga - važan izvor biološki aktivnih spojeva

Elderberry – important source of biologically active compounds

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Elders (*Sambucus spp.*) are widely distributed throughout the world. In central Europe, the most common species are black elder (*Sambucus nigra* L.) [1]. Elderberry bark, root, leaves, flower and fruits have been used particularly by the rural population as medicine and food [2]. The fruits were used traditionally as food to make elderberry wine and pies, and as a flavoring or dye. However, the consumption and use of elderberry are not very common and only a few studies have been reported. This study examined the polyphenol composition and antioxidant properties of water extracts from elderberry bark, leaves, flower and fruit. The aim of this study was also to determine the total anthocyanin content in the fruit. The total phenol content amongst the water extracts was higher in the fruit (21.55 mg GAE/g DM) and decreased in the following order: flower > leaves > bark. The total flavonoid content was higher in the flower (32.96 µg QE/g DM) and decreased in the following order: leaves > fruit > bark. Antioxidant capacity, expressed as mg TEAC/g DM measured by the radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) scavenging capacity and the phosphomolybdenum method (reducing power) was high in all observed parts of elderberry. The total anthocyanin content in fruit, determined according to the pH differential method, was 2.07 mg/g DM.

The results show that all parts of elderberry are rich in biologically active substances. These substances can be used after isolation from elderberry parts (flower, leaves, fruits, bark) as natural additives in food industry for enriching a wide variety of foods (beverages, bakery products, sweets). Accordingly, incorporation of elderberry extracts into foods could confer positive health benefits to humans.

Acknowledgements: Supported by the Project KEGA 032 SPU-4/2013.

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Izazovi prehrambene industrije danas i u budućnosti

Challenges facing the food industry today and in the future

Vlasta Piližota

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The food industry is the largest manufacturing industry in the world. In the last century, food production in the developed world has become increasingly more automated, industrialized, globalized, and characterised by larger 'players' in the market and a smaller workforce. Nowadays, there are hundreds of product categories on the market, and to compete, companies must be constantly innovative.

However, the global food and drink manufacturing industry today is facing many challenges, but also will in the future.

The challenges, issues and trends which influence food industry today, and trends expected to influence it over the next years are many: climate change, environmental impact, sustainability, food security, global economic downturn, food safety and consumer trust, obesity and diet-related illnesses, and others.

Increasingly faced with e.g. environmental challenges, natural resources shortages, financial constraints and world population increase, the food industry today also needs to constantly seek to limit waste and to improve productivity, in short, to do more with less.

Viskoznost sladovine iz heljedinog slada

Viscosity of buckwheat malt wort

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Buckwheat (*Fagopyrum esculentum*) is an important raw material for the production of cereal products for celiac disease patients, such as gluten-free beer. Malting of buckwheat is a complex process that has not been yet thoroughly investigated. One of very important technological parameters for the malting process evaluation is the viscosity of Congress wort. Different procedures of buckwheat malting were performed and the samples were taken at different stages of the malting process. For buckwheat malt quality assessment, the worts were prepared using the Congress mashing method. Total soluble solid matter (TSS), density and viscosity were determined for the worts. The values of TSS ranged from 5.2 to 7.2%, densities from 1.018 to 1.030 g·cm⁻³ and viscosity from 1.6 to 6.2 cP. For the better understanding of the hydrolysis process more detailed analyses of degree of polymerization were performed for the selected saccharides solutions. From concentration dependence of apparent specific volumes and reduced viscosity, their limiting values were estimated. Limiting values of specific apparent volumes and reduced viscosity were discussed in terms of mean molar mass and degree of polymerization of saccharides.

Higijenski dizajn pogona i opreme u prehrambenoj industriji

Hygienic design of plant and equipment in the food processing industry

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The hygienic design of the food processing plant and equipment is a design that allows for all assets to be cleaned efficiently in order to minimize the risk of any kind of hazard. It can be considered as a prerequisite program of a HACCP system. The other benefit of the hygienic design and the correct installation of the equipment is a reduction of the cost of operation, cleaning and maintenance.

In the EU, the fundamental requirements for the equipment in relation to design and manufacture are laid down in the Machinery Directive 2006/42/EC. The hygienic requirements for the food processing equipment are generic and the key points are related to the materials in contact with food, cleanability of the equipment, smooth surfaces free of imperfections and dead areas, and drainability. The EC regulation 853/2004 (General Food Hygiene) or the EC regulation 1831/2003 (Food Contact Materials) also provide requirements related to the hygienic design and state of the equipment and other surfaces. For the specific recommendations on the hygienic design or installation of the equipment and design of the processing plant, a number of sector specific standards and guidelines have been needed and issued. In the EU for example, the European Hygienic Engineering & Design Group (EHEDG) provides guidelines for different components of equipment and different food processing sectors.

The benefits of the hygienic design are clear, but do they justify the higher cost of the hygienically designed equipment? The most often stated answer is affirmative because often run times of the hygienically designed equipment can be extended, cleaning times shortened, cleaning chemicals and water reduced, maintenance costs lowered, and a longer life of the equipment can reduce return on investment. As the benefits are related to the sustainability of the processing through the reduction of water use, the term hygienic eco-design has been recently used. Current research has been aimed to provide suitable experimental results at industrial scale in the food processing sector. The environmental impact (water, energy, cleaning products, waste-water and air emissions) generated by the cleaning and disinfection of quality hygienic eco-designed equipment and surfaces is less than the standard one but in order to justify the cost of the equipment, - it needs to be quantified.

This presentation gives an overview of the key principles, trends and challenges, and examples of some of the recommended solutions in the field of hygienic design of food processing facilities and equipment.

***In vitro* evaluacija toplinski ciljanog konjugata
visoko aktivnog derivata doxorubicina**

***In vitro* evaluation of a thermally targeted conjugate
of a highly potent doxorubicin derivative**

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Doxorubicin is an anthracycline used in the treatment of many types of cancer. It intercalates into the strands of DNA to inhibit the progression of topoisomerase II, stopping the cell from replicating. The side effects, however, are severe and include neutropenia, alopecia, nausea, myelosuppression, and cardiotoxicity. High doses are needed to treat cancer cells and inadvertently harm normal cells. *n*-Butyldiacatodoxorubicin (NBD) is a doxorubicin derivative that is converted in vivo to 2-pyrrolinodoxorubicin, a ~ 1000-fold more active form. Because of its high potency, an efficient drug delivery system is needed in order to deliver NBD to the tumor site. To retain potent antitumor activity while reducing systemic toxicity, NBD was coupled to a thermally responsive macromolecular carrier based on elastin-like polypeptide (ELP) which remains in solution at physiological temperature and accumulates in the tumor site when external hyperthermia is applied. The N-terminus of ELP was modified with the cell penetrating peptide (CPP) SynB1, to facilitate cellular uptake of the ELP carrier. NBD was attached to a terminal cysteine residue of ELP by conjugation of a 6-maleimidocaproyl hydrazone derivative of NBD with an acid-sensitive linker cleavable at the lysosomal/endosomal pH, which allows controlled intracellular release of the drug. The ELP-delivered NBD inhibited MCF-7 cells growth in the nanomolar range. Inhibition of cell proliferation was enhanced two-fold as well as apoptosis, growing 3-fold when hyperthermia was applied. These results suggest that the SynB1-ELP-NBD conjugate is a promising candidate for investigating its thermally targeting properties against solid tumors in animal models.

Utjecaj kronične potrošnje taurina i kofeina na miševe koji pokazuju anksiozno ponašanje

Effects of chronic consumption of taurine and caffeine on anxiety-like behavior mice

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Energy drinks containing taurine and caffeine, reported to act as energy boosters and alertness enhancers, have become extremely appealing to young and adult consumers worldwide and show a marked increase in sales [1,2]. Recently, energy drinks intake was associated with severe pathologies [3-5]. However, the effects of prolonged energy drinks consumption on anxiety-related behaviors remain unknown. Here, we examined the effects of sustained taurine and caffeine intake on mouse anxiety-related behaviors. Two groups (n=6-7) of BALB/c male mice were exposed for 7 weeks to a control diet (CO) or to CO supplemented with taurine/caffeine (TC). Mice weights and motor coordination (as examined by the Rota rod test) showed no significant differences between groups. In the Open Field test, however, whereas no significant differences in total distance traveled were found, mice fed with TC entered significantly more and spend more time - in the center of the field, indicating reduced anxiety-like behavior. To independently evaluate anxiety-related behavioral changes, we also used the Elevated Plus Maze test. Congruently, mice fed with TC spend more time in the maze open arms, indicating reduced anxiety-like behavior. Further research should explore the involvement of chronic energy drink consumption in the modulation of emotional states.

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Acetilirana drvena celuloza kao polimerna osnova biokompozitnih materijala

Acetylated wood cellulose as polymer base of bio composite materials

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Natural polymeric materials are an interesting alternative to petrochemical products with potential application in almost all areas of human activities. However, despite the fact that the use of natural polymers based on polysaccharides, proteins and agricultural raw materials is very common, studies on the potential use of acetylated cellulose isolated from wood as bio composite materials polymer matrix are very scarce. Specifically, acetylated cellulose application is almost exclusive to preparation of membranes for desalination, medical dialysis and filtration, while the commercial application of cellulose esters in terms of structural materials is at very low level, which regularly involves the synthesis and application of mixed cellulose esters (*e.g.* cellulose acetate butyrate as material for tool handles and/or glasses frames).

Wishing to expand the field of cellulose acetate application to bio composite wood material systems, the possibilities of cellulose isolation and its acetylation from two domestic commercially meagerly used wood species was investigated in this paper. Quantitative analysis of laboratory acetylation process alongside the chemical analysis of gained product by infrared spectroscopy (FT-IR) indicates the impact of water present in cellulose structure on the values of mass increase, number of acetyl groups and the degree of acetylation. The results of the thermogravimetric analysis (TGA) confirmed thus obtained results.

Ekološki aspekti uzgoja industrijske konoplje

Ecological aspects of the industrial hemp cultivation

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Hemp (*Cannabis sativa*) is one of the oldest cultivated crops in human history and the first written record on hemp farming and usage, found in China, is estimated to be four thousand years old. Over the course of history and due to its psychoactive effects, *Cannabis* was ascended to godhood, but its usage as recreational drug resulted in prohibition of hemp growing.

Three species of *Cannabis sativa* are known: *Cannabis Sativa* planted for seeds, fiber and oil production; *Cannabis Indica* primarily grown for isolation and usage of psychoactive tetrahydrocannabinol (THC) and *Cannabis Ruderalis* characterized by higher cannabidiol (CBD) content which possesses a wider scope of medical application with no psychoactive effect.

Hemp is traditionally grown and used for textile and paper industries in recent centuries in Europe, but due to its abuse as a drug and incomplete and ambiguous interpretations on detrimental impact of THC, planting of all hemp species has been banned in most European countries during the past decades.

Results of recent studies on hemp cultivation impact on soil structure and nutrient content affected by crop rotation [1], therapeutic effects of hemp oil and seeds [2,3] and significant biomass production [4], describe hemp as one of the important and profitable crops of the future.

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Koncentracije policikličkih aromatskih ugljikovodika u zraku na različitim lokacijama u Hrvatskoj

Concentrations of polycyclic aromatic hydrocarbons in the air at different locations in Croatia

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Policiklički aromatski ugljikovodici (PAU) su onečišćenja koja mogu imati veliki utjecaj na živote ljudi zbog svojih karcinogenih i mutagenih svojstava. Izvori PAU su raznoliki, mogu biti prirodni kao što su veliki šumski požari, i antropogeni (ispušni plinovi iz industrijskih postrojenja, promet, izvori iz kućnih ložišta itd).

Cilj ovoga rada je usporediti koncentracije PAU vezanih na čestice aerodinamičkog promjera manjeg od 10 μm (PM10) na četiri lokacije u Hrvatskoj, koje se međusobno razlikuju po gospodarstvu i načina života. Uzorkovanje je provedeno u Zagrebu, glavnom gradu Hrvatske (A), planinskom mjestu s malom razvijenom industrijom u Gorskom kotaru (B), ruralnom mjestu smještenom u sjevernom dijelu hrvatske (C), te u industrijsko razvijenom području u središnjem dijelu Hrvatske (D). Uzorkovanje je provedeno mjesec dana u zimskom periodu, te mjesec dana u ljetnom periodu. Koncentracije PAU-a su analizirane pomoću tekućinske kromatografije visoke djelotvornosti (HPLC) s fluorescentnim detektorom.

Mjerene su koncentracije 9 PAU uključujući benzo(a)piren. Na svim mjernim lokacijama su koncentracije mjerenih PAU bile znatno više u zimskom razdoblju mjerenja. Tijekom zime najviša koncentracija benzo(a)pirena (BaP) zabilježena je na mjernom mjestu B i D i iznosila je oko 5 ng/m^3 , dok je najniža zimska vrijednost koncentracije BaP zabilježena za mjerno mjesto C (0,44 ng/m^3). Srednje vrijednosti koncentracije BaP tijekom ljetnog mjerenja na tri lokacije bile su niže od 0,06 ng/m^3 , dok je na lokaciji D srednja vrijednost BaP bila 0,137 ng/m^3 . Na svakoj lokaciji izračunati su omjeri pojedinih PAU kako bi se mogli procijeniti mogući izvori onečišćenja.

Optimiranje radnih parametara razgradnje natrijevog dodecilbenzen sulfonata primjenom naprednih oksidacijskih procesa

Determination of optimum working parameters of sodium dodecylbenzenesulfonate degradation based on advanced oxidation processes

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The history of Fenton chemistry dates to 1894, when Henry J. Fenton reported that H₂O₂ could be activated by Fe(II) salts to oxidize tartaric acid. Since then, Fenton and related reactions have become of great interest. In the last few decades, the importance of hydroxyl radical (HO·) reactions in waste- water treatment has been recognised and viewed as a potentially convenient and economical way to generate oxidizing species for treating chemical wastes [1].

This study reported about the decomposition of anionic surfactants (AS) based on Fenton and photo-assisted Fenton systems using UV lamp as a light source. The aim of the investigation was to optimize operating conditions that have a significant effect on sodium dodecylbenzene sulfonate (NaDBS) decomposition, AS which cannot be easily biodegradable [2,3]. The experiments were conducted at room temperature in undivided cylindrical glass cell. NaDBS determination was performed by potentiometry (titrations and direct potentiometry) using self -made PVC based surfactant sensitive electrode with hexadecyltrioctadecylammonium-tetraphenylborate ion-pair as an electroactive material [4]. For on-line monitoring (temperature and potentiometric measurement: pH-value, redox potential, NaDBS concentration) the DAQ data acquisition system was used.

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Upotreba farmerovog sjemena (FS) u suvremenoj poljoprivredi

Use of farm-saved seed (FSS) in modern agriculture

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Farmers may use seed that they have saved for their own use to grow and harvest a crop - this is known as Farm Saved Seed (FSS). It mostly refers to the harvested grain only of those self-pollinated agricultural varieties, such as wheat, soybean, and barley, that are protected by the Plant Breeders Rights legislative. Croatia urgently needs a law-regulated framework that would determine FSS as a transparent seed category. The framework should include all necessary regulations on purposes, technical standards, and transparent collecting of royalty on FSS use. Any uncontrolled FSS transaction-charged, bartered or free - causes inability to collect and control royalty on FSS. Misuse of FSS will also cause difficulties for the milling and baking industries that often set up high demands with respect to quality and exact varietal seed, as well as for producers that might not be able to sell such mixed seed to the food processing and confectionery industry. Consequently, reappearance of certain diseases (*Tilletia tritici*) will necessarily increase chemical field application, and lower germination rate of FSS might increase the required quantity of artificial manures in the soil. This is not in accordance with the recommended sustainable agricultural practice of the European Union.

Posterska priopćenja
Poster presentations

Sekcija: Kemijska analiza i sinteza
Topic: Chemical analysis and synthesis

**Ru(III) salicilaldehidato kompleksi – sinteza i interakcije
s nekim biološkim molekulama**

**Ru(III) salicylaldehydato complexes – synthesis and interactions
with some biological molecules**

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Sintetizirana su dva nova Ru(III) salicilaldehidato kompleksa. Njihova karakterizacija je izvršena elementarnom analizom, IR i UV/VIS spektroskopskim metodama. Na osnovu dobivenih podataka, određene su empirijske formule produkata: $\text{RuCl}_2\text{L} \times \text{Et}_3\text{NHCl} \times 0,1\text{Me}_2\text{CO}$ i $\text{RuCl}_2\text{L} \times \text{Et}_3\text{NHCl} \times 0,6\text{Me}_2\text{CO}$, gdje je L deprotonirani salicilaldehid, $\text{C}_6\text{H}_4(\text{O})\text{CHO}$. Podaci dobiveni spektroskopskim metodama pokazuju da se, kod oba sintetizirana kompleksa, ligand koordinira na metalni ion preko kisika karbonilne grupe i fenolnog kisika, što ove komplekse čini pogodnim prekursorima u sintezi Ru(III) kompleksa sa Šifovim bazama.

Nakon što je određen hidrolitički profil sintetiziranih kompleksa, ispitana je njihova interakcija sa DNA i proteinima seruma: albuminom i apotransferinom. Dobiveni podaci ukazuju na postojanje interakcije, što upućuje na potencijalnu biološku aktivnost sintetiziranih kompleksa.

Eksperimentalna i kvantno kemijska istraživanja ferocena supstituiranih nukleobaza

Experimental and quantum chemical study of ferrocenyl-substituted nucleobases

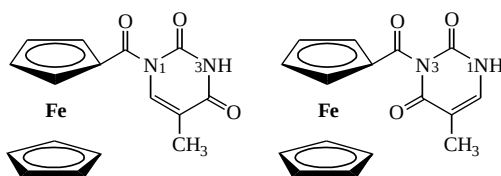
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Nucleobases substituted by ferrocenyl moiety present interesting organometallic conjugates due to their structures which incorporate both biologically and electrochemically active components. Synthetic procedures for preparation of N1- and N3-ferrocenyl substituted pyrimidine bases (thymine, cytosine) and N9-ferrocenyl substituted purine base (adenine) have been developed. The position of substitution in products has been confirmed by spectroscopy methods (NOESY-NMR, IR).

Quantum chemical calculations (DFT level of theory) have been employed to rationalize the preferential reaction of ferrocenecarbonyl chloride with N1-nitrogen atom in pyrimidine nucleobases. The calculated energy of activation for the reaction at N3-position is cca. 30 kJ/mol higher than the barrier for the corresponding reaction at N1-position. In addition, N1-ferrocenyl substituted nucleobases have been calculated more stable than their N3-substituted counterparts.



N1- and N3-ferrocenyl substituted thymine

Substitution of pyrimidine and purine bases with the ferrocenyl moiety perturbs some important intrinsic properties of the bases, such as keto-enol tautomerism and hydrogen bonding. It is expected that ferrocenyl substituted nucleobases can participate in a novel type of base pairing.

Praćenje "samo-oksidacije" cisteina u prisutnosti Cu²⁺

Monitoring of "self-oxidation" of cysteine in presence of Cu²⁺ in real-time

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The thiol functional group of the amino acid cysteine is highly sensitive to redox state, mainly due to reactivity of anionic sulphur to various oxidized agents that can form multiple types of oxidized species and can perform a countless number of physiological functions. Copper is known to being the cofactor of enzymes involved in respiration processes or in removal of reactive oxygen species. Copper ions influence the catalytic oxidation of biomolecules, thus the production of reactive oxygen species (ROS) and consequently the level of oxidative stress. Interactions of cysteine (thiols) with various transition metals have received a considerable amount of attention, but available data are too contradictory or scarce to estimate the mechanism of the proposed reaction. These include dependence of the oxidation rate of thiol compounds on pH, inertness of thiol to oxygen in aqueous alkaline solution and oxidation of aminothiols in presence of various variable-valence metals [1-5]. In this work, a novel approach to the investigation of a mechanism, kinetics and rate of oxidation of cysteine in real-time, with simple, low-cost and widely available commercial Cu-ISE, are presented. Behaviour and processes that take place near or at electrode surface are monitored and explained using electrochemical impedance spectroscopy (EIS).

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Razvoj novog potencimetrijskog senzora za određivanje anionskih tenzida

Developement of a new potentiometric sensor for detection of anionic surfactants

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Surfactants are chemical compounds with the ability to decrease the surface tension of a solvent. In the year 2012 the value of world production of surfactants amounted to 27.040 million, an increase of 6.18% is expected by the year 2017 [1]. Standard method for the determination of anionic surfactants (ASs) is MBAS method [2]. Because of the many shortcomings of MBAS method, there is a constant need to develop sensors that are cheaper and easier to use, and potentiometric sensors in this area are widely applied [3-4]. A novel potentiometric sensor based on new complex ion pair dimethyldioctadecylammonium-tetraphenylborate (DDA-TPB) [5] was developed. New sensor is sensitive, accurate, selective, rapid, simple and inexpensive. Sensor exhibited a Nernstian response for sodium dodecyl sulfate (NaDDS, 59.0 mV/decade) and sodium dodecylbenzene sulfonate (NaDBS, 59.1 mV/decade) over the range of $3 \cdot 10^{-7}$ to $8 \cdot 10^{-3}$ M for NaDDS and $4 \cdot 10^{-7}$ to $2 \cdot 10^{-3}$ M for NaDBS. Different pH values, ionic strengths and commonly used nonionic surfactants, organic anions and inorganic anions did not have a significant influence on the sensor performances or the accuracy of ASs determination.

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Spektroskopska ispitivanja derivata vitamina B6

Spectrophotometric studies of novel derivatives of vitamin B6

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The chemistry of vitamin B6 has been intensively investigated for nearly a century, which is understandable given the importance of the life processes in the body. In recent years research has focused on the synthesis and spectroscopic studies of new analogs of vitamin B6, which can be used in human medicine for recovery from organism poisoning by organophosphorus compounds. The UV/VIS absorption spectra of the synthesized derivatives of vitamin B6 were recorded in aqueous solutions of different pH values. The spectra were recorded on the Specord 200 spectrophotometer (Analytik Jena AG) at the temperature of 25 °C. pH readings were fitted using the appropriate amount of hydrochloric acid (0.2 M), sodium hydroxide (0.2 M) and Britton-Robinson buffer. Britton-Robinson buffer was prepared by mixing equimolar amounts of phosphorous (0.04 M H₃PO₄) acetate (0.04 M CH₃COOH) and boric acid (0.04 M H₃BO₃). The absorption spectra of aqueous solutions of the test compounds changed by altering the pH of the solution. In the acidic medium there are two peaks, one at about 280-293 nm and the other at 330 nm. By increasing the pH the second peak is lost, and the first ranges at about 270-274 nm with the emergence of a new peak at about 378-380 nm.

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Biokatalitička redukcija prokiralnih ketona

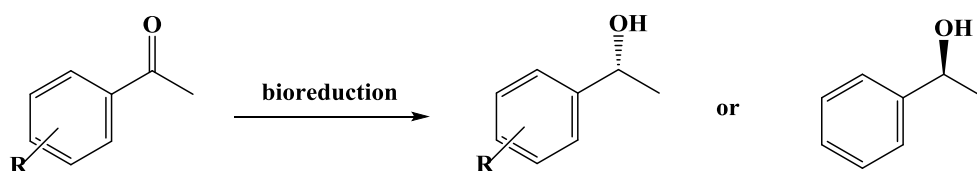
Biocatalytic reduction of prochiral ketones

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Biotransformations are a worthy alternative when trying to substitute a conventional chemical reaction by a greener method in organic chemistry. There are numerous chemical and biological methodologies available to obtain chiral alcohols. Asymmetric reduction of prochiral ketones is one of the most important and practical reactions for producing chiral alcohols which can be transformed into various functionalities, to synthesize industrially important chemicals such as pharmaceuticals, pesticides, pheromones, flavors, fragrances and industrial fine chemicals. In the last decade various examples of reduction of prochiral ketones to chiral alcohols have been reported directly using parts of plants as biocatalysts. Various plants, such as apple (*Malus pumila*), carrot (*Daucus carota*), cucumber (*Cucumis sativus*), onion (*Allium cepa*), potato (*Solanum tuberosum*), radish (*Raphanus sativus*) and sweet potato (*Ipomoea batatas*) were used as the biocatalysts. Here we report the results of reduction of acetophenone analogues by pea (*Pisum sativum*) and beans (*Phaseolus vulgaris*).



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Kompleksiranje bakra(II) s tiocianatnim ionima u prisutnosti površinski aktivnih tvari

Complexation of copper(II) with thiocyanate ions in the presence of surfactants

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Dodatak površinski aktivnih tvari (PAT) primjenjuje se za poboljšanje ekstrakcijskih i spektrofotometrijskih metoda. Kompleksi koji uz metal i kompleksirajući reagens uključuju i prisutnost molekula PAT pokazuju povećanje molarne apsorptivnosti i batokromni pomak apsorpcijskog maksimuma u odnosu na kompleks koji nastaje bez prisutnosti PAT.

U ovom radu spektrofotometrijskim mjerenjima ispitano je kompleksiranje bakra(II) s tiocianatnim ionima u vodenoj otopini uz dodatak neionske površinski aktivne tvari Tritona X-100 (TX-100).

Bez dodatka TX-100 ispitivani sustav pokazuje maksimum apsorpcije pri 360 nm, a dodatkom TX-100 dolazi do povećanja intenziteta apsorpcije Cu-SCN kompleksa kao i do pomaka apsorpcijskog maksimuma prema većim valnim duljinama.

Crveno-smeđe obojeni tiocianatni kompleks bakra koji nastaje u prisutnosti TX-100 kod pH = 1 maksimalno apsorbira pri 406 nm i slijedi Lambert-Beerov zakon u području koncentracije bakra(II) od 5×10^{-5} do 5×10^{-4} mol dm⁻³, a molarna apsorptivnost iznosi 2590 dm³ mol⁻¹ cm⁻¹.

Ispitani sustav može se primijeniti kao "spot test" za određivanje prisutnosti bakra u raznim uzorcima.

Elektroanalitička karakterizacija i određivanje imidazolijevih dipeptida karnozina i anserina

Electroanalytical characterization and determination of imidazol dipeptides carnosine and anserine

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Carnosine and anserine are dipeptides that are contained in the skeletal muscles or brains of vertebrates in high concentrations. These substances may function to reduce muscle fatigue and improve learning ability because of an anti-oxidative effect and buffering capacity due to the presence of an imidazole group.

L-Carnosine (β -alanyl-L-histidine) is a dipeptide composed of β -alanine and L-histidine, which performs multiple biological functions including pH buffering, anti-oxidation, anti-glycation, anti-aging, and chelation of divalent metal cations [1]. Anserine (β -alanyl-N-methylhistidine) is an N-methylated analogue of carnosine found mainly in fish and birds. Anserine has similar properties to carnosine in many aspects but is mainly found in non-mammalian species.

Carnosine and anserine can be determined in biological materials by means of HPLC using fluorescent [2] and electrochemical detection [3], capillary electrophoresis [4] and microchip electrophoresis [5].

In these investigations carnosine and anserine were potentiometrically studied, single and in a mixture. Their acid-base properties were studied by use of potentiometric titrations that were carried out in aqueous and nonaqueous solvents. The generated potentiometric data were used for defining buffering capacities (buffer strength) of both dipeptides and for determination of the corresponding species distribution diagrams.

The experimental data were compared with an appropriate theoretical curve in which the unknown properties (sample concentration, dissociation constant) are optimized. By using Solver (Excel), the values for those variables can be found that minimize the sum of the squares of the differences between the theoretical and experimental curve by using the least-squares criterion to fit a theoretical curve to the experimental data [6].

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Sinteza i antioksidacijska aktivnost derivata dipikolinske kiseline

Synthesis and antioxidant activity of dipicolinic acid derivatives

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Dipicolinic acid mono and di-derivatives were synthesized, namely thiosemicarbazides, oxadiazoles, thiadiazoles and triazoles and their structures were confirmed utilizing different methods. New compounds were evaluated for their antioxidant activity utilizing four methods, DPPH scavenging activity, phosphomolybdenum method, iron chelating and reducing power method, and their activity was compared to the starting compound, dipicolinic acid. Some of the synthesized compounds were proven to possess an excellent antioxidant activity compared to dipicolinic acid itself and ascorbic acid as standard compound.

Određivanje ukupnog sadržaja fluorida u čajevima korištenjem fluoridne ionsko-selektivne elektrode

Determination of total fluoride content in teas by using fluoride ion-selective electrode

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The total fluoride content was analyzed in 30 tea samples. The analyzed samples were chamomile (*Matricaria chamomilla*), green tea (*Camellia sinensis*) and mint (*Mentha piperita*) in tea bags and bulk, purchased at local supermarkets and market places in Split, Croatia. The tea samples were digested in a microwave in nitric acid and hydrogen peroxide mixture.

Potentiometric determination by using fluoride ion-selective electrode was applied in this work. Average F⁻ concentration in all tested samples was 0.183±0.161 mg L⁻¹. In order to get a better insight into the fluoride content in different plant samples, a One-Way ANOVA (program R) was used for statistical data analysis. Concentration of F⁻ followed normal distribution. F⁻ concentrations ($P < 0.001$) were higher in the bulk samples (0.354±0.039 mg L⁻¹) than in tea bag ones (0.111±0.007 mg L⁻¹) for mint. F⁻ content was not statistically different among plant samples. Green tea samples had total content in range from 0.0163 to 0.509 mg L⁻¹. Chamomile samples had total content in range from 0.0001 to 0.4367 mg L⁻¹ with the highest recorded dispersion. When the total fluoride contents are compared to the data of those in tea infusion, it can be seen that the biggest fluoride extraction occurs during green tea brew [1].

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Primjena novog potenciometrijskog senzora za određivanje anionskih tenzida u otpadnim vodama

Application of a new potentiometric sensor for determination of anionic surfactants in wastewater

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Anionic surfactants are used in detergent formulations for laundry, personal care products, household cleaning products and industry. Their wide application leads to water pollution and thus endangers the flora and fauna [1]. Due to a lack of standard methods for the determination of anionic surfactants [2] new sensors, which are less expensive and miniaturized, are being continuously developed for easier and wider use [3-5].

A new *screen-printed* potentiometric microsensor (SPMS) for the determination of anionic surfactants (ASs) is based on the dimethyldioctadecylammonium-tetraphenylborate (DDA-TPB) ion pair as a sensing material. Sensor is accurate, inexpensive, simple and very sensitive. DDA-TPB was used for the end-point detection during the potentiometric titrations of low levels of ASs in wastewater. Solutions of cetylpyridinium chloride (CPC) concentrations down to $5 \cdot 10^{-5}$ M were used as a titrant. Standard addition method was used for checking the precision and accuracy of measurements, and it provided very satisfactory results with recoveries between 98.3 to 102.0 % in pure AS solutions and 99.0 to 114.5 % in wastewater. Standard spectrophotometric method Methylene Blue Active Substances (MBAS) was used as control for comparison of the results obtained with new sensor.

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Elektropolimerizacija pirola na Mg leguri u svrhu zaštite biorazgradivih implantata

Electropolymerization of pyrrole on Mg alloy for biodegradable implant application

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Many reasons make magnesium and its alloys the best potential materials for biodegradable implants: (i) magnesium is an essential element to humans and beneficial for bone strength; (ii) magnesium degrades in physiological solutions; and (iii) the mechanical properties of magnesium are similar to those of natural bone. Unfortunately, magnesium is very susceptible to corrosion in physiological solutions and its mechanical properties decrease before the new tissue has healed.

Various surface treatments have been applied to magnesium and its alloys to improve their corrosion resistance and the lifetime of implants. It has been also found that pre-treatment methods are very important for the protection of magnesium against corrosion. Pre-treatment methods remove the passive oxide layer that forms easily due to the high reactivity of Mg and has a detrimental effect on coating adhesion and uniformity.

Because of its relatively easy preparation from aqueous solution and stability at oxidized state, polypyrrole and its derivatives are reported to be among the most important candidates for corrosion protection. In this study, the polymeric coating (polypyrrole) was formed on the magnesium alloy by electrochemical polymerization from aqueous solution of sodium salicylate. The protection efficiency of the polymeric coatings was investigated in a simulated physiological solution (Hanks' solution) using voltammetry and electrochemical impedance spectroscopy methods. The structural characteristics of the surface coatings were investigated by the FTIR technique.

Elektrokemijska karakterizacija (1E)-1-N-{[4-(4-{[(E)-N-(4-aminofenil) karboksiimidoil]fenoksi}butoksi) fenil] metiliden} benzen -1,4-diamin

Electrochemical characterization of (1E)-1-N-{[4-(4-{[(E)-N-(4-aminophenyl) carboxyimidoil]phenoxy}butoxy) phenyl] methilidene} benzene -1,4-diamine

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Oxido-reduction properties of a newly synthesized Schiff base were investigated by cyclic voltammetry and differential pulse voltammetry. Measurements were conducted in a three electrode voltammetric cell in a non-aqueous medium. Glassy carbon was used as a working electrode, platinum wire as counter electrode and non-aqueous Ag/Ag⁺ electrode as a reference electrode. Inert atmosphere was accomplished by system purging with high purity argon Ar 5 ($\phi_{Ar} = 99,999\%$), before each measurement.

Cyclic voltammograms revealed one oxidation and one reduction peak of the investigated Schiff base ($E_{p,a} = 0,44$ V and $E_{p,k} = 0,39$ V), which increased both with increasing concentration ($c = 3,1 \cdot 10^{-5}$ mol dm⁻³... $1,25 \cdot 10^{-4}$ mol dm⁻³) and with scan rate ($v = 50...300$ mV/s) [1, 2]. Differential pulse voltammetry showed one oxidation peak $E_{p,a} = 0,41$ V, which also increased with rising concentration [3].

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**Termodinamički studij CdCl_2 u smjesi 2-propanol (5 mas. %) + voda
primjenom potencijometrije**

**Thermodynamic study of CdCl_2 in 2-propanol (5 mass %) + water mixture
using potentiometry**

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The potential difference (pd) measurements (E) are reported for galvanic cell without liquid junction: $\text{Cd}(\text{Hg})$ (l, sat.) | $\text{CdCl}_2(b)$ in Z | $\text{AgCl}(\text{s})$ | $\text{Ag}(\text{s})$ at different temperatures and various CdCl_2 molalities (b) in aqueous mixture of 2-propanol (containing 5 mass % 2-propanol). From these values and using literature data for stability constants of the chlorocadmium complexes, the values of the standard pd of the cell were obtained at each temperature. These values served to calculate the standard thermodynamic quantities for the cell reaction, and also mean molal activity coefficients of CdCl_2 . The corresponding thermodynamic results are discussed and compared with literature data.

Sekcija: Kemijsko i biokemijsko inženjerstvo
Topic: Chemical and biochemical engineering

Ostaci monenzina u tkivu jetre pilića nakon primjene lijeka

Monensin residues in the liver of broiler chickens following drug administration

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In intensive poultry production, anticoccidial drugs are used and authorised as feed additives for poultry for the prevention and treatment of coccidiosis, an infectious disease caused by several species of *Eimeria* and *Isospora* protozoa that predominantly affects young animals [1]. Monensin is a polyether carboxylic ionophore coccidiostat agent commonly used on poultry farms and is authorised for use at a concentration of 100-125 mg kg⁻¹ of feed in chickens for fattening with a withdrawal period of 3 days [2]. The electrostatic property of monensin may cause contamination of feed mill production lines after milling medicated feed, because it is impossible to ensure completely contamination-free production [3]. Kinetic studies on various animal species have shown that the highest levels of monensin residues are excreted in the liver [4]. In the European Union, the maximum residue levels (MRL) for monensin in the liver have been set at 8 µg kg⁻¹ [2]. In this study, monensin residues are determined in the liver tissue of broilers (n=25) treated with feed medicated with monensin concentrations of 325 mg kg⁻¹ for 21 days, which is three times the maximum authorised concentration level. The broilers were killed and liver tissue was collected for 13 days after the end of administration. Residues of monensin were measured using liquid chromatography-tandem mass spectrometry (LC-MS/MS) with electrospray ionisation. The validation parameters of the method were determined in accordance with the criteria of Commission Decision 2002/657/EC [5]: LOD, limit of detection 1.70 µg kg⁻¹; LOQ, limit of quantification 6.73 µg kg⁻¹; CC_α, limit of decision 9.35 µg kg⁻¹; recovery 99.5%. The maximum concentrations of monensin of 58.7 µg kg⁻¹ were measured on the first day of post-treatment. Concentrations dropped below the MRL value (7.05 µg kg⁻¹) on the 4th day and below the LOQ value (2.86 µg kg⁻¹) on the 5th day of post-treatment. On the 7th day after the end of treatment, monensin levels declined below 1 µg kg⁻¹. The results of the study confirmed the rapid excretion of monensin from liver tissue even when it is administered to broilers at concentrations three times higher than the authorised maximum content.

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Koncentracije aflatoksina M1 u sirovom kravljem mlijeku u zimskim mjesecima 2014

Aflatoxin M1 concentrations in raw cow's milk during the winter months of 2014

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Mycotoxins aflatoxins produced by mould species of the genus *Aspergillus* are known as harmful mutagenic, teratogenic, carcinogenic and immunosuppressive agents [1]. The presence of aflatoxin B1 in the feed of lactating animals leads to the contamination of milk with the hydroxyl-metabolite aflatoxin M1 (AFM1). AFM1 is a stable molecule in raw and processed milk and is unaffected by the process of pasteurisation or treatments used during cheese production [2]. As far as temperature and moisture are concerned, climatic conditions in tropical and subtropical regions favour the growth of the toxigenic *Aspergillus* [3]. However, long periods of high temperature and long-lasting drought in summer favour the development of these moulds in feed in other climatic regions [4]. The aim of this study was the assessment of AFM1 concentrations in a total of 427 raw cow's milk samples collected in January (n=143), February (n=151) and March (n=133) of 2014 from farms around Croatia. AFM1 concentrations were measured using a competitive enzyme immunoassay. The method has been validated in accordance with the criteria of Commission Decision 2002/657/EC and the validation parameters were (ng kg⁻¹): LOD, limit of detection 22.2; LOQ, limit of quantification 34.2; CC_β, detection capacity 33.0. AFM1 levels in the milk were measured in the following range (ng kg⁻¹): 2.81-211.4. Mean AFM1 levels measured in the three months were (ng kg⁻¹): January 11.5, February 15.6, March 10.5. The highest concentration of 211.4 ng kg⁻¹ was determined in February. AFM1 levels exceeded the LOQ value (34.2 ng kg⁻¹) in only 12 samples out of 427 analysed samples. In a total of 8 milk samples (1.87%), AFM1 concentrations exceeded the European Union maximum residue permitted amount of 50 ng kg⁻¹ [5]. The low incidence of elevated AFM1 in the milk indicates a low incidence of contaminated complementary foods, which were used on only a few farms during the winter months of 2014. Seasonal variations of AFM1 concentrations have been previously confirmed in Croatia, with an increase in concentrations during winter when lactating cows were fed with greater amounts of mixed supplementary feedstuff compared to the summer [6].

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Oksidacijska desulfurizacija dizelskog goriva

Oxidative desulfurization of diesel fuel

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Poboljšanje kvalitete motornih goriva s obzirom na ekološke karakteristike kontinuirano je usmjereno prema smanjenju sadržaja sumpora, što je moguće postići različitim postupcima desulfurizacije. U tom smislu, proces oksidacijske desulfurizacije razvijen je kao alternativa/ dodatak postojećem procesu hidrodiesulfurizacije (HDS) te nudi nekoliko prednosti u odnosu na klasični HDS. To su blagi reakcijski uvjeti, atmosferski tlak i temperatura do 100°C, uz veću reaktivnost aromatskih spojeva i činjenicu da se u ovim procesima ne koristi vodik. Druga važna prednost je sposobnost pretvaranja (oksidiranja) tiofenskih spojeva u sulfokside i sulfone, koji su jako polarni spojevi i mogu se lako ukloniti procesom ekstrakcije ili adsorpcije. U novije vrijeme istražuju se procesi potpomognuti ultrazvukom u cilju povećanja brzine reakcije i ukupne izmiješanosti reakcijskog sustava.

U okviru eksperimentalnog rada, provedeno je istraživanje ultrazvukom potpomognutog procesa oksidacije realnog dizelskog goriva pri različitim uvjetima. Istražen je utjecaj procesnih parametara: temperature u rasponu 50-90 °C, snage ultrazvuka od 40-80 W i vremena reakcije od 10-30 min. Nakon procesa oksidacije provedena je ekstrakcija rafinantne faze dimetilformamidom i metanolom, te je istražen utjecaj solvent odnosa. Analiza ukupnog sumpora nakon procesa oksidacijske desulfurizacije provedena je na WDX-XRF uređaju.

Kinetika sušenja katalizatora u sušioniku s fluidiziranim slojem

Fluid bed drying kinetics of catalysts

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U ovom je radu istraživana kinetika sušenja katalizatora u fluidiziranom sloju. Mjerenja su provedena u laboratorijskom sušioniku pri različitim brzinama strujanja zraka, temperaturama te visinama sloja čvrstih čestica različitih veličinskih frakcija. Preliminarna istraživanja uključila su karakterizaciju sferičnih čestica katalizatora. Izmjerena je tvrdoća i gustoća čestica te raspodjela veličina pora. Morfologija čestica katalizatora definirana je SEM analizom dok je sastav utvrđen EDS analizom.

Rezultati su pokazali da temperatura, brzina strujanja zraka te visina sloja čvrstih čestica utječu na kinetiku sušenja. Veća brzina sušenja odgovara većim temperaturama i povoljnijim hidrodinamičkim uvjetima te manjoj visini sloja čvrstih čestica. Kinetika sušenja opisana je pomoću četiri matematička modela. Procijenjeni su koeficijenti prijenosa topline i tvari, te efektivni difuzijski koeficijent. Parametri modela i procijenjena prijenosna svojstva korelirani su uvjetima provedbe procesa. Na temelju izvedenih korelacija može se procijeniti kinetička krivulja sušenja pri drugim uvjetima provedbe procesa.

**Ravnoteža kapljevina-kapljevina u sustavu
ugljikovodik – piridin – [C₆mmpy][Tf₂N]**

**Liquid-liquid equilibrium for the system
hydrocarbon – pyridine – [C₆mmpy][Tf₂N]**

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Liquid–liquid extraction is one of the alternative methods that can be used for denitrification of FCC gasoline and diesel fuel. Extraction with ionic liquids as selective solvents makes the separation process ecologically acceptable due to the nonvolatility of ionic liquids as well as their complete regeneration.

Liquid–liquid equilibrium for the systems hydrocarbon – pyridine – [C₆mmpy][Tf₂N] has been experimentally determined at the atmospheric pressure at 25 °C. Three paraffin hydrocarbons (*n*-hexane, *n*-heptane and *i*-octane) and one aromatic hydrocarbon (toluene) have been selected, since FCC gasoline mostly consists of paraffins. Toluene was selected because aromatic hydrocarbons are soluble in ionic liquids, and pyridine is a representative of nitrogen compounds. Besides the equilibrium curves, the tie lines were also experimentally determined. Equilibrium data were described with NRTL and UNIQUAC models. Distribution coefficients and selectivities of ionic liquid were evaluated. Both of them decrease with increasing concentration of pyridine. The extraction efficiency is higher for the three-component systems with paraffins. For the model solution which consists of all selected compounds plus thiophene a decrease in extraction efficiency was observed with respect to three-component system.

Primjenjivost *n*-heksadekana pri regeneraciji ionskih kapljevin

The applicability of *n*-hexadecane in regeneration of ionic liquids

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Lately, particular importance is given to investigations connected with possibility of application of ionic liquids in a diverse industrial processes regarding the new methods and replacement of many volatile organic solvents. The purpose is to minimize waste generation and negative impact on the environment as well. The possibility of application of ionic liquids in different industries is initialized by their specific properties like non-volatility, stability and many others. These properties present ionic liquids as a promising alternative to environmentally undesirable volatile organic solvents. The "green character" of ionic liquids makes their multiple usage and regeneration possible. For these reasons, in this work the possibility of regeneration of diverse ionic liquids, one based on pyridine, while others on imidazolium, was investigated. They were contaminated in the desulfurization process of model solution representatives diesel fractions. The ionic liquids regeneration was provided by liquid-liquid extraction with *n*-hexadecane as a selective solvent, which was chosen on the basis of its physical properties. Mass ratio of ionic liquid and selective solvent was 0.5. Nuclear magnetic resonance (NMR) confirmed that the dibenzotiofene, as the only pollutant in tested ionic liquids, was completely removed.

Nova otapala za ekstrakciju tiofena iz smjese sa *n*-heksanom

New solvents for extraction of thiophene from the mixture with *n*-hexane

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Desulphurisation and denitrification of petrol and diesel fuels is one of the leading problems in the oil and petrochemical industry. Today, more and more scientists are researching ways to adapt existing processes and develop new technologies that would ensure the desired quality of liquid fuels. Liquid-liquid extraction by eco-friendly solvents is especially interesting because extraction as a process can be carried out at mild process conditions. The use of ionic liquids in extraction desulphurization processes is the object of a large number of investigations. Lately, ionic liquid mixtures and deep eutectic solvents are used as selective solvents. Ionic liquids and deep eutectic solvents possess excellent properties that satisfy the majority of the needs that have to be fulfilled when choosing a solvent. Apart from them being nonvolatile, a key factor for extraction is to ensure a high selectivity towards the components that need to be extracted from the liquid mixture and to achieve high mass transfer rates.

In this work the possibility of using a mixture of two ionic liquids at different mass ratios ([C₂mim][EtSO₄]-[C₅mim][Tf₂N]; [C₂mim][EtSO₄]-[C₆mmPy] [Tf₂N]; [C₂mim][EtSO₄]-[bmim][Tf₂N] and [C₆mmPy] [Tf₂N]- [bmim][Tf₂N]) and also the use of a deep eutectic solvent choline chloride:glycerol (1:2,n) as selective solvents in the separation of thiophene and *n*-hexane by liquid-liquid extraction were investigated. Raffinate of higher purity was gained by using a ionic liquid mixture that had higher fractions of the more effective ionic liquid in the mixture. Ionic liquids and their mixtures were more adequate solvents for the separation of thiophene and *n*-hexane than deep eutectic solvent choline chloride:glycerol.

Usporedba fizikalno-kemijskih i primjenskih svojstava motornog benzina i njegovih mješavina s bio-butilnim alkoholima

Comparison study of physico-chemical and application properties of motor gasoline and its blends with bio-butyl alcohols

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Uz bioetanol i etilne ili metilne estere uljane repice koji se trenutno najviše koriste kao biokomponente za motorna goriva, razmatraju se i druge mogućnosti, a jedna od njih su i butilni alkoholi proizvedeni iz biomase kao što su *n*-butanol i izobutanol. Iako je u usporedbi s bioetanolom njihova biotehnoška proizvodnja mnogo zahtjevnija, brojne prednosti pri upotrebi u motorima s unutarnjim izgaranjem učinila su ih vrlo atraktivnim alternativnim izvorom energije. Do nedavno, butilni alkoholi proizvedeni iz biomase nisu se ozbiljnije razmatrali kao biogorivo ili komponente za namješavanje s motornim benzinom prvenstveno zbog kompliciranog i financijski neisplativog procesa njihove proizvodnje koji se naziva Aceton-Butanol-Etanol (ABE) fermentacija. Međutim, novi pomaci u tom procesu u zadnjih nekoliko godina učinili su ga konkurentnim na komercijalnoj razini. Iz tog su razloga brojne tvrtke u SAD i Europi svoja postojeća postrojenja za proizvodnju bioetanola počela prenamjenjivati za proizvodnju butilnih alkohola. U ovom radu, eksperimentalno je istraženo područje primjene butilnih alkohola kao komponenti za namješavanje s motornim benzinom s ciljem izbjegavanja nepovoljnog utjecaja na rad motora. U tu svrhu priređene su mješavine motornog benzina sa *n*-butanolom i izobutanolom u širokom rasponu volumnih udjela od 5 do 50 %. Priređenim mješavinama ispitana su glavna fizikalno-kemijska i primjenska svojstva kao što su kemijski sastav, svojstva isparljivosti (destilacijske karakteristike, tlak para po Reid-u), oktanski broj, kinematička viskoznost i indeks refrakcije. Dodatno, postojeća ¹HNMR metoda za određivanje strukturno-grupnog sastava motornog benzina, modificirana je s ciljem određivanja sastava priređenih mješavina s butilnim alkoholima. Razvijena metoda pokazala se vrlo brzo, pouzdanom i korisnom, posebice za mješavine s većim udjelom alkohola, gdje se standardizirana kromatografska tehnika (PIONA) pokazala ograničenom. Dobiveni rezultati pokazuju da butilni alkoholi znatno mijenjaju fizikalno-kemijska svojstva motornog benzina, pogotovo u smjesama s udjelom alkohola većim od 20 vol. %. U zakonski propisanim okvirima (do 7 vol. %), butilni alkoholi utječu povoljno na ispitana svojstva posebice na svojstva isparljivosti te na linearno povećanje oktanskog broja za mješavine motornog benzina s izobutanolom.

Mješljivost poli(metil-metakrilat) i polilaktid mješavina

Miscibility of poly(methyl methacrylate) and polylactide mixtures

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U ovom radu ispitivano je ponašanje mješavina poli(metil-metakrilata) (PMMA) i polilaktida (PLA) različitog sastava. Za pripravu mješavina korišten je komercijalni PLA, dok je PMMA sintetiziran reakcijom radikalne polimerizacije metil-metakrilata. U gnjetilici Brabender pripravljene su mješavine poli(metil-metakrilata) i polilaktida (PMMA/PLA) sastava (mas. %): 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, 0/100. Dobivene mješavine korištene su za prešanje ispitnih epruveta. Provedena je karakterizacija dobivenih polimernih mješavina. Metodom kontaktnog kuta ispitana su svojstva površine pripremljenih uzoraka. Termogravimetrijskom analizom i diferencijalnom pretražnom kalorimetrijom (DSC) ispitana su toplinska, a dinamičko-mehaničkom analizom mehanička svojstva uzoraka. Homopolimeri pokazuju hidrofilnu prirodu i imaju slične vrijednosti kontaktnog kuta (79° i 82°). Zabilježena je značajna razlika u toplinskoj postojanosti homopolimera, pri čemu PLA podliježe razgradnji u jednom, a PMMA u dva stupnja. Dobra mješljivost u PMMA/PLA mješavinama potvrđena je DSC mjerenjima gdje je zabilježeno jedno staklište, smješteno između staklišta homopolimera. Rezultati ispitivanja dinamičko-mehaničkom analizom ukazuju da mješavine u području do 60 °C uglavnom imaju znatno više vrijednosti modula pohrane (E') u odnosu na homopolimere, što znači veću žilavost, elastičnost i sposobnost deformiranja. Budući da dodatak PLA značajno mijenja mehanička svojstva PMMA u temperaturnom području do 60 °C, može biti pogodan za njegovu modifikaciju za određene namjene.

Utjecaj hrapavosti površine stjenke mikroreaktora na profil strujanja u sustavu kapljevina-kapljevina

Effect of surface roughness on flow profile of liquid-liquid system in a microreactor

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Microreactors provide very large interfacial surface-to-volume ratio, effective mass and heat transfer and easier process control compared to classic reactor. Due to these advantages they are widely applied for multiphase reactions. Microreactors were primarily used for gas-liquid systems [1] and lately they have become very interesting for application in liquid-liquid systems [2]. To insure the optimal conditions for performing multiphase reaction in microreactor, hydrodynamic conditions must be optimised. Slug flow and parallel flows can be formed by introducing two immiscible liquids into microreactor. According to Dessimoz et al. [3] flow pattern formation depends on linear velocity of both phases, ratio of the phases, fluid transport properties, microreactor channel geometry and construction material.

In this work analysis of the liquid-liquid flow profile was performed. Six organic solvents (dichloromethane, ethyl acetate, diethyl ether, hexane, chloroform and toluene) as one phase together with water as second phase were introduced in the microreactor. Two microreactors with internal volume of $V = 4 \text{ mm}^3$ and $V = 6 \text{ mm}^3$ with different surface roughness were used to analyse effect of surface roughness on flow profiles. The flow profiles in the microchannel were monitored by microscope. The analysis based on specific dimensionless numbers (Reynolds, Capillary and Weber) was performed to get the better insight in process dominant for specific flow profile formation.

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Hidrotermička razgradnja masti, ugljikohidrata i proteina u sjemenkama suncokreta nakon obrade subkritičnom vodom

Hydrothermal degradation of fats, carbohydrates and proteins in sunflower seeds after treatment with subcritical water

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Subcritical water is an alternative and environmentally friendly processing medium with interesting applications in many fields of research. Its ability to degrade natural biopolymers (cellulose, protein etc.) into smaller, usually water soluble products (sugars, amino acids etc.) has found to be quite useful, especially in waste and biomass processing technologies. Nevertheless, for composition and food processing, these degradation reactions can have a negative effect on the food structure itself, resulting in an altered structure with lower quality or even formation of toxic compounds. It is therefore important, that these hydrothermally induced reactions are studied in more detail in order to know how and when they occur.

In this study, the hydrothermal degradation of fats, carbohydrates and proteins in subcritical water was observed. For the raw material, sunflower seeds were chosen. The grinded material was subjected to subcritical water in a temperature range from 130 °C to 240 °C for a time period of 5 min to 120 min. After treatment, the hexane soluble (oil) and water soluble phases (proteins and carbohydrates) were collected and analyzed for products of hydrothermal degradation. Oil stability was investigated by analyzing the content of free fatty acids that could have been formed during treatment with subcritical water. Amount of FFAs present in oil samples was determined using gas chromatography. The water soluble phase was analyzed for the presence of any formed amino acids. Furthermore, the total carbohydrates were analyzed to evaluate any loss of carbohydrates during the treatment. Total amino acids and carbohydrates were determined using the ninhydrin and phenol/sulfuric acid spectrophotometric methods, respectively.

Results showed that the obtained oils were the most stable macronutrient present in the sunflower seeds. Only small amount of FFAs was formed during hydrothermal processing. Proteins seemed to be less stable than the oils, whereas the carbohydrates have proven to be very susceptible to hydrothermal degradation, since total carbohydrate concentration rapidly decreased even at the lowest observed temperature. This decrease in total carbohydrates indicates that foods containing high amounts of carbohydrates should not be exposed to subcritical water at too high temperatures for too long, otherwise the product is quickly degraded to non-edible or even toxic products, such as furfurals and organic acids.

Strukturna svojstva i ionska vodljivost nanokompozitnih polimernih elektrolita

Structural properties and ionic conductivity of nanocomposite polymer electrolytes

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U ovom radu istraživao je utjecaj dodatka litijevog montmorilonita (LiMMT) na strukturu i ionsku vodljivost nanokompozita na osnovi poli(etilen-oksida) (PEO). PEO je često korišten polimer za pripremu polimernih elektrolita zbog svojih dobrih elektrokemijskih i mehaničkih svojstava. Ipak, visok stupanj kristalnosti PEO-a smanjuje njegovu ionsku vodljivost. Smanjenje stupnja kristalnosti postiže se dodatkom anorganskih čestica PEO-u stvarajući polimerne elektrolite sa poboljšanim elektrokemijskim svojstvima.

Utjecaj dodatka LiMMT-a na strukturu PEO-a ispitivan je primjenom raspršenja X-zračenja pri malom kutu (SAXS) i infracrvene spektroskopije s Fourierovom transformacijom (FTIR). Rezultati SAXS metode ukazuju na interkalaciju polimernih lanca između slojeva montmorilonita, odnosno nastanak nanokompozitne strukture. FTIR analiza pokazuje da dodatak punila narušava helikoidalnu strukturu PEO-a u nanokompozitima, odnosno njegovu kristalnost. Diferencijalnom pretražnom kalorimetrijom (DSC) potvrđeno je da dodatak punila smanjuje kristalnost PEO-a. Ionska vodljivost nanokompozita određena je elektrokemijskom impendancijskom spektroskopijom (EIS). EIS pokazuje značajan porast ionske vodljivosti pri sobnoj temperaturi dodatkom LiMMT-a te je definiran optimalan udio LiMMT-a.

Termooksidativno starenje polimerom modificiranog bitumena

Termoxidative aging of polymer modified bitumen

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Bitumen aging resulting in hardening of bitumens and embrittlement, both in application and in service, contributes greatly to the deterioration of paving application. Aging is a very complex process of bitumen; BIT and the complexity increase when polymers are involved in polymer modified bitumens, PmBs.

This paper presents an investigation of termoxidative aging of PmB prepared from bitumen and five active and inactive polymers. Aging of the PmBs was performed using the Rolling Thin Film Oven Test, RTFOT. The PmBs were characterized by means of Fourier Transform Infrared Spectroscopy, FTIR, differential scanning calorimetry, DSC, and dynamic shear rheometry, DSR. It was found that the effect of aging on the chemistry and rheology of the PmB was influenced by the bitumen and was strongly dependent on the characteristics of the polymer. The rheological changes of styrene-butadiene-styrene, SBS, modified bitumens, were attributed to polymer degradation and bitumen oxidation with the aging. In the case of ethylene vinyl acetate, EVA, modified bitumens' changes after aging were mainly due to the oxidative hardening of the bitumen and the degradation of crystal region in the EVA PmBs. However, they have been proven to be very stable for active polymers under aging due to the formation of chemical bonds.

Kompatibilizacija mješavina termoplastičnog poliuretana/polipropilena s dva različita blok kopolimera

Compatibilization of thermoplastic polyurethane/polypropylen blends with two different block copolymers

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The blending of polymers provides a powerful route for obtaining materials with improved property/cost performance. Since most blended polymers are immiscible, compatibilization is required to obtain maximum synergy.

The blends of thermoplastic polyurethane, TPU and isotactic polypropylene, iPP are incompatible because of large differences in polarities between the nonpolar crystalline iPP and polar TPU and high interfacial tensions. The miscibility between TPU and iPP in a blend can be improved by addition of compatibilizers.

In this research, blends of TPU and iPP were modified with two styrene-ethylene/butylene-styrene, SEBS, triblock copolymers with the aim of improving the compatibility and in particular thermal stability of the TPU/iPP blends. The compatibilizers involved an unfunctionalized, SEBS and one functionalized grade containing maleic anhydride, SEBS-g-MAH, grafted to the midblock. The effects of the compatibilizers were evaluated by on thermal stability of the TPU/iPP blends by thermogravimetric analysis, TGA. The samples of neat homopolymers and their blends without and with 5 wt. % of compatibilizers were prepared using a laboratory twin-screw extruder with various rations of TPU and iPP, followed by classic molding.

Based on the results it can be concluded that both block copolymers as compatibilizers improve miscibility of TPU/iPP blends. According to TGA results, the addition of compatibilizers enhances thermal stability.

Utjecaj toka kapljevine na mehanizam i brzinu nukleacije boraksa u kristalizatoru s jednim i dvama turbinskim miješalima

Influence of the fluid flow patterns on borax nucleation mechanism and nucleation rate in a single and dual turbine impeller crystallizer

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The aim of this work was to investigate the influence of fluid flow pattern in the crystallizer on the nucleation mechanism and rate of disodium tetraborate decahydrate (borax) in the process of batch cooling crystallization. Examinations were performed in the crystallizer of 15 dm³ with *liquid level* to tank *diameter ratio* (H/d_T) of 1.3 and diameter ratio impeller to tank (D/d_T) of 0.33. The fluid flow patterns in the crystallizer were generated by axial and radial turbine impellers and by their different dual combinations. Impeller speed ensured the state of complete suspension in the system for all configurations used ($N = N_{JS}$).

Crystallization was carried out by cooling of the mother liquor from the saturation temperature of 30 °C by the rate of 6 °C h⁻¹. Concentration of solution was measured in line by the means of Na ion-selective electrode, while the onset of nucleation i.e. metastable zone width was detected from the changes of concentration values. Mechanism and nucleation rate were determined according to Mersmann's nucleation criterion. In order to gain the complete insight into the overall fluid flow in the crystallizer, the photographs of the flows were taken and simulations by *VisiMix 2000 Turbulent* package were made. Power consumption over the process time for all impeller configuration used was also measured.

Obtained results indicated that overall fluid flow in the crystallizer, developed by single impeller or by interaction of flows generated by each of impellers in dual impeller system, has a different impact on the achievement of the complete suspension state. This directly reflects on the nucleation mechanism and nucleation rate as well as on the power consumption.

Analiza lokalne osjetljivosti parametara integriranog modela membranskog bioreaktora

Local sensitivity analysis of integrated membrane bioreactor model

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Membrane bioreactors (MBRs) consist of the combination of biological processes (typically activated sludge process) with membrane technologies which are being applied when high quality effluents are required. Over the last decades, membrane technologies alone or in combination with biological processes (i.e. MBRs) have been successfully applied for municipal and industrial wastewater treatment. MBR-based technology is a complex physico-chemical and biological system with numerous interactions between the process variables. For design and better understanding of this complex system mathematical modelling is a very useful tool. According to literature, there are several integrated models describing both physical and biological processes taking part in MBRs with some simplifications. But there is still a big challenge in developing an integrated model that is able to describe the biological nutrient removal, formation/degradation of soluble microbial products and physical separation.

In this work one-to-one local sensitivity analysis was applied to define the most important parameters of integrated activated sludge model 2d and soluble microbial product (ASM2d-SMP) model proposed by Cosenza et al. [1]. Model includes 19 biological state variables and 79 parameters (kinetics, stoichiometric, physical and fraction-related). By simulating the described mathematical model with one and three percent parameters value increase/decrease, the key regulation points of the model are detected. Obtained results facilitate future experiment planning and can be a good starting point for model reduction.

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Reološka i toplinska karakterizacija nanofluida

Rheological and thermal characterization of nanofluids

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Da bi se povećala energetska učinkovitost izmjenjivača topline, potrebno je poboljšati toplinska svojstva konvencionalnih nanofluida. Znatno poboljšanje toplinskih svojstava moguće je postići suspendiranjem nanočestica u kapljevinama koje se uobičajeno primjenjuju u izmjenjivačima topline.

Stoga su u smjese voda – etilen glikol te voda – glicerol, primjenom ultrazvučne sonde, dispergirane nanočestice aluminijske (III) oksida u rasponu koncentracija 0,3-1,4 vol %. Stabilnost suspenzija ispitana je nefelometrijskom metodom korištenjem uređaja 3 u 1 – PTN.

Nakon postizanja stabilnosti suspenzija, izmjerena je njihova gustoća i viskoznost te su određena reološka svojstva. Također, određena su i toplinska svojstva pripremljenih suspenzija: koeficijenti toplinske vodljivosti, specifični toplinski kapacitet i temperaturna vodljivost.

Pripremljeni nanofluidi i bez dodatka aditiva pokazuju stabilnost u razdoblju od jednog mjeseca, imaju svojstva newtonskih fluida s neznatnim povećanjem gustoće i viskoznosti u odnosu na bazni fluid. Toplinska svojstva nanofluida poboljšavaju se s povećanjem volumnog udjela nanočestica za oba bazna fluida.

Primjenom nanofluida u pločastom izmjenjivaču topline, izračunat je koeficijent prijelaza i prolaza topline pri različitim protocima i koncentracijama nanofluida. Koeficijent prijelaza i prolaza topline nanofluida povećava se s povećanjem volumnog udjela nanočestica kao i poboljšanjem hidrodinamičkih uvjeta u izmjenjivaču topline.

Utjecaj metala iz okoliša na kemijske promjene maslinovog ulja

Impact of metals from the environment on chemical changes of virgin olive oil

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Metal contamination sources have been increasing everywhere, with many documented cases of metal toxicity in mining industries, foundries, smelters, coal burning power plants and agriculture. Heavy metals such as cadmium, copper, lead, chromium and mercury are major environmental pollutants, and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons. Heavy metal accumulation in the soil is of concern in agricultural production due to its effects on plants and their metabolic activities, possible bioaccumulation, food safety and human health. Humans and other living organisms are a part of the biogeochemical cycle of metals and are directly exposed to their impacts. Virgin olive oils are high quality food with a balanced triglyceride composition that provides their nutritional and protective value. The ideal composition of olive oil does not automatically imply a positive effect on health. Namely, during ripening, harvesting and processing of olives, especially during oil storage, oxidation processes can occur on triglycerides and can significantly affect the quality and safety of virgin olive oil. These chemical changes in virgin olive oil are provoked by exposure to air, heat and light but these processes can be catalysed at increased contents of heavy metals.

This paper presents the results of lead, copper and iron content in 81 samples of virgin olive oil. Results are correlated with chemical parameters that indicate oxidation processes. Concentrations of lead ranged from <0.001 to 1.13 mgPb/kg, moreover in 21 samples the lead content was above the maximum permissible level. Concentrations of copper and iron were between <0.001 to 6.56 mg Cu/kg and <0.001 to 22.7 mg Fe/kg. In 49 samples (60.5%) concentration of metals was above the permissible level, and in 59% of these samples the oxidative changes have been observed. The results indicate a correlation between increased concentrations of metals and oxidation of the virgin olive oil.

Dijagnostika i optimiranje rada industrijskih procesa

Industrial process diagnostics and optimisation

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U industrijskim procesima velik broj varijabli potrebno je održavati unutar strogo definiranih granica kako bi postrojenja radila stabilno, a kvaliteta produkata bila zadovoljavajuća. Edukacija i obuka inženjera, nadziranje, dijagnostika i optimiranje procesa imaju ključnu ulogu u osiguranju da postrojenje zadovoljava radne zadatke, ekonomično radi i zadovoljava standarde zaštite okoliša.

Primjenom suvremenih softverskih alata moguće je statistički analizirati rad procesa i sustava za vođenje, identificirati dinamičke modele procesa i regulacijskih krugova te optimirati parametre sustava za vođenje. Time se postiže stabilnije vođenje procesa i veća kvaliteta produkata.

Na temelju rada regulacijskih krugova identificira se model procesa, optimiraju parametri regulatora, izvode prilagodljive i napredne metode vođenja bazirane na modelu procesa. Optimiranjem standardnog i naprednog sustava za vođenje moguće je stabilizirati proces i omogućiti rad postrojenja bliže procesnim, sigurnosnim i ekonomskim ograničenjima.

Kao primjer, analiziran je i optimiran dio postrojenja fluid-katalitičkog krekinga. Dinamičko vladanje procesa opisano je empirijskim dinamičkim modelima primjenom metoda identifikacije procesa. Pri optimiranju primijenjena je metoda reduciranih gradijenata. Na temelju analize optimiran je rad regulacijskih krugova temperature, razine i protoka.

Nakon primjene optimiranih parametara u sustavu za vođenje ostvareni su kvalitetniji rad i stabilnije vođenje. Također je određen broj regulacijskih krugova prebačen iz ručnog u automatski način rada, a riješen je i problem osciliranja kod pojedinih regulacijskih krugova te prekomjernog gibanja i trošenja regulacijskih ventila. Na taj način smanjuju se operativni troškovi i poboljšava kvaliteta proizvoda.

Sekcija: Prehrambena tehnologija i biotehnologija
Topic: Food technology and biotechnology

Aromatski profil ploda jagode sorte "Clery" iz vrgoračkog uzgojnog područja

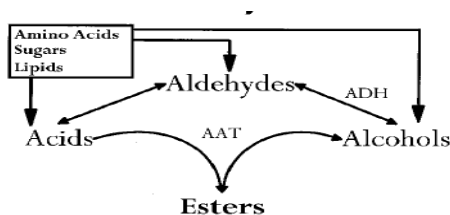
Aroma profile of strawberry fruit cultivar "Clery" from Vrgorac growing area - Croatia

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Fresh strawberries are popularly consumed worldwide for their delectable flavour and high nutritional content [1]. Sugars and acids are responsible for the sweetness and tartness of the fruit [2]. The Vrgorac area in Croatia is well known for its high quality strawberry production. The headspace volatiles were isolated by headspace solid phase microextraction (HS-SPME) using fiber coated with the layer of Polydimethylsiloxane/Divinylbenzene (PDMS/DVB). Obtained samples were analyzed by gas chromatography and mass spectrometry (GC-MS) on HP-5MS column. The main compounds of strawberry fruit headspace were esters: Methyl butanoate (14.5%), Methyl hexanoate (12.6%), Ethyl butanoate (8.9%) and Butyl butanoate (6.9%). Esters are the most important group of volatile compounds responsible for the aroma of strawberry fruit. The primary enzyme believed to be responsible for ester production is alcohol acyltransferase (AAT). Alcohol dehydrogenase (ADH) is another enzyme that is involved in synthesis of aroma volatiles in strawberry fruit [2]. However, the study of a larger number of samples from various years of production supports the results obtained by this first screening.



Ester Biosynthesis in strawberry fruit.

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Isparljivi spojevi lista masline sorte *Oblica*

Volatile compounds of olive leaves cultivar *Oblica*

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Maslina (*Olea europaea* L.) je jedna od najvažnijih voćki u mediteranskim zemljama, gdje pokriva otprilike oko 8 milijuna hektara, što čini gotovo 98% svjetskog usjeva. Kemijski sastav isparljivih spojeva maslinovog lista ovisi o nekoliko faktora, kao što su: sorta masline, sezona, stanje lišća, geografski i klimatski uvjeti [1]. U ovom radu analiziran je kemijski profil isparljivih spojeva uzorka suhog lista masline sorte *Oblice* dobiven hidrodestilacijom (HD) i mikroekstrakcijom vršnih para na krutoj fazi (HS-SPME) koristeći vlakna s prevlakama: PDMS/DVB (polidimetilsiloksan/divinilbenzen, 65 µm) i DVB/CAR/PDMS (divinilbenzen/karboksen/polidimetilsiloksan, 50-30 µm). Analiza izoliranih isparljivih spojeva lista masline provedena je vezanim sustavom plinska kromatografija-spektrometrija masa (GC-MS) koristeći kolonu HP-5MS. Najzastupljeniji spojevi dobiveni HD metodom su: 3-etenilpiridin (27.4%), benzaldehid (6.3%), (*E,E*)-heksa-2,4-dienal (0.4%), (*E*)-hept-2-enal (0.4%) i heptanal (0.3%). Glavni spojevi dobiveni HS-SPME metodom koristeći vlakno sa PDMS/DVB prevlakom su: α-kopaen (31.5%), nonanal (10.9%), (*E*)-heks-2-enal (6.3%), (*Z*)-β-ocimen (4.2%) i heks-3-en-1-ol (2.2%). Glavni spojevi vršnih para izolirani HS-SPME metodom sa DVB/CAR/PDMS prevlakom su: α-kopaen (11.1%), (*E*)-heks-2-enal (8.4%), 2-etilheksanol (5.4%) i propan-1-ol (5.2%). Rezultati ovog rada pokazuju komplementarnost upotrebljenih preparativnih tehnika za potpunu karakterizaciju isparljivih spojeva lista masline. Općenito, isparljivi spojevi lista masline različitih sorti pokazali su antioksidacijsko, antibakterijsko, antigljivično djelovanje koje može biti korisno za farmaceutsku i kozmetičku industriju [1].

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Sastav isparljivih spojeva meda od vrtnog čubra (*Satureja hortensis* L.)

Volatile compounds of summer savory (*Satureja hortensis* L.) honey

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The summer savory is a commonly used spice and medicinal plant containing essential oil rich in carvacrol, γ -terpinene, lower amount of α -terpinene, *p*-cymene and several other compounds [1]. Its flowers provide nectar that can be collected by the bees to obtain honey. In the present study, unifloral sample of summer savory (*Satureja hortensis* L.) from plantation in Poland was analyzed. The volatiles were extracted from the sample by two different methods to obtain full profile: ultrasonic solvent extraction (USE) and headspace solid-phase microextraction (HS-SPME), and analyzed by gas chromatography-mass spectrometry (GC-MS). The main compounds of summer savory headspace were terpenes: hotrienol, safranal, α -terpineol, *trans*- and *cis*-linalool oxides, lilac aldehyde isomers I-III, linalool and *p*-menth-1-en-9-al. Benzene derivatives were also present in the headspace: benzaldehyde, phenylacetaldehyde, 1-methyl-2-(2-propenyl)benzene, *p*-cymen-8-ol and ethyl benzoate. Less volatile compounds from this group predominated in the USE extract: methyl syringate, benzoic acid and vanillic acid. Additionally, norisoprenoid 4-hydroxy-3,5,6-trimethyl-4-(3-oxo-1-butenyl)-cyclohex-2-en-1-one and terpene acetoxylinalool were present along with several hydrocarbons. All the relevant compounds have been present in several other honey types, thus may be useful only as non-specific markers of botanical origin. The composition of volatile profiles is different from the composition of essential oil obtained from the herb. However, it is very similar to a volatile profile of the honey obtained from winter savory (*Satureja montana* L.), a plant from the same family. Among the identified volatile compounds, hotrienol with sweet and floral aroma was predominant in the headspace of winter savory, followed by smaller percentages of 4-methoxybenzaldehyde, *trans*- and *cis*-linalool oxides. Methyl syringate and syringaldehyde were the main compounds of the extract. The presence of safranal, α -terpineol, lilac aldehyde isomers I-III in the headspace of summer savory and absence of syringaldehyde in the extract may help to differentiate it from winter savory.

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Antioksidacijska aktivnost i koncentracija ukupnih fenola bijelog vina Žilavka

Antioxidant activity and total phenol concentration of white wine Žilavka

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In this paper, total phenol concentration and antioxidant activity of Herzegovinian white wines was determined. Eighteen commercially available white wine samples made from domestic cultivar Žilavka (vintage 2011) were analyzed. Total phenol content was determined spectrophotometrically according to the Folin-Ciocalteu method using gallic acid as a standard. Two distinct methods were used to assess the antioxidant activity of tested wines: spectrophotometric monitoring of reduction of free radical DPPH and Briggs-Rauscher (B-R) oscillating reaction method. Total phenol concentration in wine samples varied from 249.3 mg/L to 801.1 mg/L expressed as mg of gallic acid equivalent per litre of wine determined from a standard calibration curve. The antioxidant capacity obtained by DPPH method ranged from 28.8% to 70.2%. In most cases, the results obtained for both, DPPH and B-R method, confirmed the fact that wines with higher total phenol content have stronger antioxidant activity.

**Izolacija i karakterizacija hlapljivih i nehlapljivih fitokemikalija
iz naranče (*Citrus sinensis* L.)**

**Isolation and characterization of volatile and non-volatile phytochemicals
from orange (*Citrus sinensis* L.)**

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Citrus sinensis L. belongs to Rutaceae family. The following study was aimed to identify volatile and non-volatile phytochemicals isolated by different methods from dried orange peel. Volatiles were isolated by hydrodistillation in Clevenger type apparatus as well as by petrolether extraction in Soxlet apparatus and analysed by GC/MS. The volatile oil as well as petrolether extract contained more than 90% monoterpene limonene. Other minor compounds, such as: monoterpenes (α - and β -pinene, sabinene, ocimene, etc.); sesquiterpenes (β -caryophyllene, α -copaene, β -elemene, valencene, etc.); alcohols (linalool, α - and β -terpineol); esters (neryl acetate, geranyl acetate, ethyl linoleate etc.) and others were also identified. The MeOH extraction of non-volatile phytoconstituents was performed after petrolether extraction in Soxlet apparatus as well as by the alkaline (KOH) extraction of the peels. The non-volatile compound obtained by crystallization was identified as hesperetin, the flavanoid aglycone of hesperidin. Limonene and hesperetin were analysed using spectroscopic methods and tested for their antioxidant and acetylcholinesterase activity.

Prešanje i ekstrakcija superkritičnim CO₂ lješnjakovog, orahovog i chia ulja

Pressing and supercritical CO₂ extraction of hazelnut, walnut and chia seed oil

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In edible oil production it is very important to find an appropriate method to recover the oil from the seeds. The amount and quality of extracted oils are crucial for determining feasibility of commercial production. Recently, interest in the use of continuous, mechanical screw presses to recover oil from oilseeds arose. However, screw pressing will not extensively replace solvent extraction in commodity oilseeds. Oil extraction using supercritical fluids is an alternative method to replace conventional industrial process such as pressing and solvent extraction. Supercritical fluid extraction is still relatively new and is not widely used on the commercial scale for the extraction of edible oils mainly due to very high investment costs for equipment. But when considering industrial application, it is essential to provide research on the fundamentals of the supercritical processes. Accordingly, the aim of this work was to evaluate the oil extraction process from hazelnut, walnut and chia seeds by screw pressing followed by extraction with supercritical CO₂. In obtained oils, the oil quality parameters such as peroxide value, free fatty acids, insoluble impurities, moisture content, iodine value, saponification value, *p*-anisidine value and Totox value were determined. The residual oil in the press cake was totally extracted by supercritical CO₂ in newly designed and built supercritical fluid extraction system. Tocopherol content of pressed oil and oil extracted by supercritical CO₂ were compared.

**Vitamin E u biljnim uljima određen RP-HPLC metodom
uz UV detekciju**

**Vitamin E in vegetable oils determined by RP-HPLC method
with UV detection**

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Vitamin E is the general term used to describe a group of eight natural isomers, which form (along with vitamin A, D and K) the group of fat soluble vitamins. Vegetable oils are one of the most important dietary sources of vitamin E which, as antioxidant, prevents oil rancidity during storage, thus prolonging its shelf-life. Among eight natural isomers belonging to this vitamin, α -tocopherol is the most active in vivo and the most represented in vegetable oils of green plants. Vitamin E presence in vegetable oils ranges from 1 mg/100 g to 162 mg/100 g [1], depending on the oil type, production process, freshness and storage conditions. The aim of this work was to determine concentrations of α -tocopherol in various edible vegetable oils. Rapid reverse-phase high-performance liquid chromatography method (RP-HPLC) with PDA detector developed by Gimeno et al. [2] was used for determination. Fourteen edible vegetable oil types were analysed. Some of them, like sunflower and rapeseed oil, are widespread and commercially available, while others attracted scientific curiosity just recently. Data on their composition are, therefore, scarce. Sunflower and chestnut oil had the highest amount of α -tocopherol, while amounts in linseed and chia oil were below the level of detection. Large differences in the content of α -tocopherol have been found between fresh oil samples and stored ones, which has especially been noted in sunflower oil.

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Iskorištenje nusprodukata voća za obogaćenje kaša od jabuka

Utilization of fruit by-product for the enrichment of apple puree

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Apple and apple products are one of the major fruit and fruit products consumed all over the world. In 2012, Croatian apple production exceeded 110 000 tons, which means that over 10 000 tons were processed in various apple products [1]. This growth has in turn generated several hundred tons of waste (25–30% solid waste) during the processing of apple products, such as apple juice, jelly and cider, among others. Often only 20% is retrieved as animal feed and the remaining 80% goes to landfill, is incinerated or is sent to composting sites resulting in the release of greenhouse gases [2]. Due to health and environmental awareness, sustainable food production and value addition of agro-industrial wastes are the principal issues in the agro and food processing industry.

Apple by-products, especially apple peel, are excellent sources of natural antioxidants, such as catechins, procyanidins, caffeic acid, phloridzin, phloretin glycosides, quercetin glycosides and chlorogenic acid, among others. In this study we used apple peel powder as an ingredient for the enrichment of apple puree. Next to apple peel powder (APP) addition (3%), sugars were also added (1 and 5% of glucose, fructose, sucrose or trehalose), and influence on apple puree phenols (TPC) and antioxidant activity (AA) was studied. Sugar addition, especially trehalose, had a significant impact on the preservation of apple polyphenols. In freeze-dried samples, the addition of lower proportion (1%) of trehalose had the highest impact on polyphenol preservation. The highest levels of polyphenols in frozen purees were measured in the samples with the addition of disaccharides (S and T). Antioxidant activity exhibits a significant correlation ($p < 0.05$) with polyphenols in both frozen and freeze-dried samples. Apple purees, enriched with APP, were higher in phenolics and antioxidant activity than in purees without APP. Better use of the by-product can provide benefits to the apple production, and fruit and vegetable industry as a whole, as well as solutions for environmental concerns associated with waste disposal. The results indicate that APP could be considered as an alternative polyphenol source or specialty food ingredient for food products or selected functional foods and nutraceuticals.

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Stabilnost pigmenata u liofiliziranoj kaši cikle tijekom skladištenja

Pigment stability in freeze-dried red beet puree during storage

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The red-purple betacyanins comprise the major part of pigments in beetroot, and of all pigments betanin comprises 75%-95%. Vulgaxanthin I and II are yellow coloured components of the beetroot colourings known as betaxanthins. The aim of this study was to investigate the stability of red beet pigments betalains and colour change in freeze-dried puree during 2 years of storage at room temperature. Red beet puree was acidified (pH from 6.5 to 3 and 5) with 10% solutions of ascorbic (AA) or citric acid (CA). Content of betacyanins as betanin and betaxanthins as vulgaxanthin I was determined by spectrophotometer. Total colour difference from the fresh puree was used to measure the colour change. Betacyanins concentration in fresh red beet puree, acidified with CA (81.6-82.8 mg 100g⁻¹) and AA (79.9-81.2 mg 100g⁻¹), did not significantly change in comparison with fresh red beet puree at pH 6.5 (83.2 mg 100g⁻¹). Acidification caused a decrease of the vulgaxanthin (1.38 in fresh red beet puree to 1.15-1.17 in the samples with CA, and to 1.11-1.25 in the samples with AA). Betacyanins and betaxanthins did not degrade at any pH after freeze-drying. After 1st year of storage red beet puree pigments showed less stability in samples acidified with AA and CA at pH 3 (46.3-48.4 mg 100g⁻¹ of betacyanins). Betacyanin and betaxanthin degradation rates, after 2nd year of storage, were increased in all samples. The lowest total colour change of puree after freeze-drying and storage had the sample acidified with AA at pH 5 (17.9).

Polifenolni spojevi u starim kultivarima jabuka iz Hrvatske

Polyphenolic compounds in old apple varieties from Croatia

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Apples are often used in diet because of their availability all year round and represent a significant source of various nutrients. They are a good source of bioactive polyphenolic compounds as well. There are few data about polyphenols in old, ancient apple varieties that used to be cultivated in the past. That is polyphenolic compounds in old apple varieties from Croatia were studied in this work (crvenka, pisanika, ledenara, adamova zvijezda, slavonska srčika, wild apple). Polyphenolic compounds were extracted by using ultrasonic bath. Extraction solvents were 80% methanol (polyphenols from apple flesh), and acidified methanol (0.1% hydrochloric acid) (polyphenols from peel). Total polyphenols were determined by using the Folin-Ciocalteu method and total anthocyanins by using the pH-differential method. The results showed that old apple varieties have high amount of polyphenolic compounds in the peel (from 2150 mg kg⁻¹ fresh weight in wild apples to 5387 mg kg⁻¹ FW in pisanika) and in the flesh (from 198 mg kg⁻¹ FW in crvenka to 5068 mg kg⁻¹ FW in wild apples). Wild apples can be highlighted among all the other investigated apples due to a high total polyphenol content in the flesh which is 86 to 96 % higher than in the flesh of other investigated apples. Furthermore, significant amounts of anthocyanins were found in the peel of red coloured apples (crvenka, pisanika). In conclusion, old apple varieties can be considered as a significant source of polyphenols, especially wild apples. The overall results showed the need to preserve and protect these old varieties because they represent a significant source for horticultural biodiversity.

Utjecaj dodatka disaharida na hlapljive tvari liofilizirane kaše višnje

Influence of disaccharide addition on volatile compounds of freeze-dried sour cherry puree

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The most important volatile compounds responsible for aroma profile of sour cherry are benzaldehyde, benzyl alcohol, 2-phenyl ethanol, eugenol, 2-hexenal, α -ionon and β -ionon. The aim of this study was to determine the influence of disaccharides (sucrose, maltose and trehalose) and their amount (3.7%, 7.1% or 13.3%) on key volatile compounds (benzaldehyde, benzyl alcohol and 2-hexenal) of freeze-dried sour cherry puree. Sugars and their amount had influence on investigated volatile compounds. Control sample (freeze-dried sour cherry puree without sugar addition) contained 856.1 $\mu\text{g/kg}$ of benzaldehyde, 3.92 mg/kg of benzyl alcohol and 15.58 $\mu\text{g/kg}$ of 2-hexenal. Samples with addition of maltose (13.3%) and trehalose (7.1%) had the highest amount of benzaldehyde (871.34 and 937.51 $\mu\text{g/kg}$, respectively). In comparison to control sample, all samples with sugar addition had lower amount of benzyl alcohol. Among samples with sugar addition, the highest amount of benzyl alcohol had samples with addition of maltose (3.7%), 3.19 mg/kg and all samples with trehalose addition, ~ 3.0 mg/kg . Samples with addition of maltose (13.3%) and trehalose (7.1% and 13.3%) had the highest amount of 2-hexenal (16.99, 17.45 and 18.96 $\mu\text{g/kg}$, respectively).

Krioprotektorsko djelovanje β -glukana iz zobí na miofibrilarane proteine govedeg mesa

Cryoprotective effect of oat β -glucans on beef myofibrillar proteins

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Cryoprotective effects of oats β -glucans on beef myofibrillar proteins after frozen storage were investigated by the use of differential scanning calorimetry (DSC). Influence of frozen storage on texture profile analysis (TPA) parameters, instrumental colour parameters and cooking loss of beef myofibrillar proteins were also investigated. Beef myofibrillar protein samples were prepared from beef meat (mainly lat. *musculus* psoas major), mixed with oat β -glucans ($w = 0 - 6\%$), quickly frozen and stored for 30 days at $-30\text{ }^{\circ}\text{C}$. Onset temperature of transition (T_o), peak thermal transition (T_p), endset temperature of transition (T_e) and denaturation enthalpy (ΔH) were evaluated. Peak (T_p) thermal transition temperatures of beef myofibrillar proteins showed a shift to higher values with the increase of mass fraction of β -glucans. Denaturation enthalpies (ΔH) of beef myofibrillar proteins showed increase with the increase of mass fraction of oat β -glucans. Instrumental colour parameters (lightness (L^*), redness (a^*), yellowness (b^*) and whiteness ($L^* - 3b^*$) of beef myofibrillar proteins were significantly ($P < 0.05$) affected by the addition of oat β -glucans. Hardness, gumminess and chewiness increased significantly ($P < 0.05$) and cooking loss decreased significantly ($P < 0.05$) by the addition of oat β -glucans. Cohesiveness and springiness of beef myofibrillar gels were not significantly ($P > 0.05$) affected by addition of oat β -glucans. Increase in peak thermal transition (T_p), denaturation enthalpies (ΔH), some TPA and instrumental colour parameters indicate possible cryostabilisation of beef myofibrillar proteins with the addition of oat β -glucans.

**Reološka svojstva čokoladnih masa tijekom skladištenja – utjecaj
mliječnih komponenata**

**Rheological properties of molten chocolate masses during storage – influence
of milk components**

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When finished chocolate mass is used for production of chocolate based products, it is often produced in large quantities, stored in molten condition at 50 – 55 °C and spent in smaller quantities during a maximum period of 30 days. It is well established in scientific literature that chocolate components have a significant influence on rheological properties. However, this influence during storage has not yet been elucidated. The aim of this research was to investigate the influence of milk components (spray-dried milk powder, cream powder and sweetened condensed milk) on rheological properties of chocolate during 30-day storage. The results showed that sweetened condensed milk had the highest impact on decrease of yield stress and plastic viscosity stability during storage. Chocolate produced with the addition of spray-dried milk powder and cream had the highest yield stress and plastic viscosity during storage.

Ekstrakcija aktivnih tvari iz lucerne

Extraction of active compounds from Alfalfa plant

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The common name of the herb Alfalfa (*Medicago sativa*) is Lucerne. It is a valuable plant grown mainly for animal feed and is rich in protein, minerals, vitamins (A, B, C, D, E, K), carotene, coumarins, alkaloids and secondary metabolites of plants [1]. In folk medicine, this herb is used in alternative herbal treatments [2]. The extract from the leaves of Alfalfa has a positive, multidirectional impact on human body. It increases the level of estrogen, prevents atherosclerosis, helps blood circulation and strengthens immunity [1]. In our work, the optimal extraction conditions for the isolation of active compound from Alfalfa were determined. Conventional extraction is the most commonly used method for isolation of valuable compounds from natural materials.

Conventional extraction was performed using aqueous solutions of acetone and ethanol with different composition (25, 50, 75 % (v/v)) and pure solvents acetone, water and 96% ethanol. Ethanol and acetone are both approved for the use in food industry as volatile solvents for extraction of valuable compounds. For the purpose of comparison, active compounds were extracted also by conventional Soxhlet apparatus using hexane as solvent. The extracts were analysed on the content of total phenols. Furthermore, the DPPH radical scavenging activity of extracts was determined.

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**Fizikalna i kemijska svojstva kukuruznih ekstrudata obogaćenih
prahom rajčice i askorbinskom kiselinom**

**Physico-chemical properties of corn extrudates enriched with
tomato powder and ascorbic acid**

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Due to the complex composition of extruded products, extrusion leads to a change in ingredients and to their interactions. Therefore, in order to produce products of satisfactory quality and nutritional value, it is necessary to know composition and properties of ingredients, as well as the influence of the extrusion process. The aim of this research was to investigate the influence of tomato powder addition to corn grits at levels 4, 6 or 8 % and ascorbic acid (AK) addition at levels 0.5 and 1% on hardness and the expansion of the extrudates. Mathematical models that describe the influence of additives on mentioned properties were also determined. The extruded products were also tested for total polyphenol content (PF) by micro Folin-Ciocalteu method and antioxidant activity (AA) by ABTS method. The extrusion was done at two temperature regimes: 135/170/170 °C and 100/150/150 °C. Lower temperature regime led to increased hardness and the expansion of extrudates. On the other hand, the addition of tomato and AK led to decreased hardness and the expansion at both temperature regimes. The addition of tomato increased PF and AA compared with pure corn extrudates. Greater degradation of PF and AA was at a lower temperature regime. High correlation between PF and AA was demonstrated at both extrusion temperatures. The addition of AK led to higher PF and AA values prior and after extrusion.

Protočna stripping kronopotenciometrija kao metoda karakterizacije polifenola u uzorcima crnih vina

Flow-through stripping chronopotentiometry as a method of characterisation of polyphenols in samples of red wine

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Vino je tradicionalno alkoholno piće, a kultura pijenja vina prisutna je u cijelom svijetu. Crveno vino bogato je polifenolnim spojevima koji imaju pogodan učinak na zdravlje ljudskog organizma. Protočna stripping kronopotenciometrija je elektroanalitička metoda kod koje se analit deponira iz otopine na radnu elektrodu pri određenom potencijalu ili struji, a zatim se nakon određenog vremena elektroliza prekida i provodi se otapanje deponiranog analita s površine radne elektrode. Ova elektrokemijska metoda primjenjuje se za određivanje anorganskih spojeva. Cilj ovog rada je pokazati moguću primjenu protočne stripping kronopotenciometrije kao brzu, selektivnu i jednostavnu metodu karakterizacije polifenola u uzorcima crvenih vina. Analizirano je pet različitih crnih vina sa područja Republike Hrvatske. Rezultati količine ukupnih polifenola dobiveni protočnom stripping kronopotenciometrijom su u korelaciji sa standardnom metodom za određivanje ukupnih polifenola Folin-Ciocalteu.

Karakterizacija djevičanskih maslinovih ulja sorte *Oblica* na temelju hlapivih tvari

Characterisation of *Oblica* virgin olive oils based on their volatile compounds

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Virgin olive oil is obtained from fresh and undamaged olive fruits (*Olea europaea* L.) by mechanical procedures [1] and it is characterized by a delicate and unique flavour highly appreciated by consumers [2].

The characteristic aroma of olive oil depends on the volatile compounds. The studies on the characterization of volatile compounds of virgin olive oils indicated that the major contributors of olive oil aroma were C6 aldehydes and alcohols. The C6 compounds (aldehydes, alcohols and esters) are enzymatically produced from linoleic and linolenic acids through the lipoxygenase (LOX) pathway [3].

Oblica is the main Croatian autochthonous variety and presents more than 60% of total olive trees. In the present study, the volatile profile of *Oblica* virgin olive was established using solid-phase microextraction (SPME) with DVB/CAR/PDMS fibre coat followed by gas chromatography-mass spectrometry (GC-MS) analysis. Predominant headspace compounds were: (*E*)-hex-2-enal (63,5%), (*Z*)-hex-3-enal (6,5%), 3-ethylocta-1,5-diene (two isomers: 7,1%; 5,5%), hexanal (4,4), pentan-3-one (2,5%), pent-1-en-3-one (1,7%) and α -copaene (1,1%).

In comparison with oils of Turkey varieties *Ayvalik* and *Memecik*, it can be concluded that there are some differences in composition of volatile compounds. The amount of the main volatiles found in tested oil is quite different to oils of Turkey varieties where the amount of (*E*)-hex-2-enal was 9,24% for *Ayvalik* oils 25,8% for *Memecik* oils. In *Ayvalik* olive oil headspace, hexanal was predominant (14,3%).

The results showed that the aroma compounds accumulate differently, depending on the varieties which indicate a close relation with the activity of an enzyme that is genetically determined.

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[3] Angerosa et al., Journal of Chromatography A 1054 (2004) 17-31.

Ekstrakcija konopljinog ulja (*Cannabis sativa* L.) superkritičnim CO₂

Supercritical CO₂ extraction of hemp (*Cannabis sativa* L.) seed oil

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Through Croatian history hemp was grown and had a large share in the industrial production. Hemp is fully usable with a large range of products, but has been unfairly neglected in the recent decade either because of the great similarities with Indian hemp or because of interest lobbies. The oil obtained from hemp seeds has great nutritional properties. Fractionation of the oil is very important for making products with physical or nutritional properties of interest in the food industry. Hemp (*Cannabis sativa* L.) seed oil fractionation with supercritical CO₂ at different conditions of temperature and pressure was studied. Hemp seed oil was fractionated into few fractions collected at different time intervals during extraction. Fractionation was performed at following temperatures: 40 and 60 °C and at pressures 300 and 400 bar. The objective of this work was to evaluate the concentration of tocopherols, fatty acids and chlorophyll *a* and *b* in different fractions of hemp seed oil obtained at different extraction process conditions. The composition of hemp seed oil obtained with supercritical CO₂ was compared with the hemp seed oil extracted by *n*-hexane.

Utjecaj procesa fermentacije s imobiliziranim stanicama kvasca na kemijski sastav i količinu biogenih amina u vinu

Effect of immobilized yeast cells fermentation on chemical composition and biogenic amine content in wine

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Biogenic amines are well known organic nitrogenous compounds with low molecular weight, which are formed from precursor amino acids, mainly by lactic acid bacteria during malolactic fermentation in wine making. They could negatively affect the wine quality and their presence in high concentrations is a health risk for sensitive individuals. The aim of this research was to determine the chemical composition and biogenic amine content in wines made from grape varieties *Merlot* and *Syrah* (*Vitis vinifera* L.) from Kutjevo vineyards, located in the eastern part of continental Croatia. Wines were produced in 2012 by cold maceration and fermentation with immobilized yeast cells.

The obtained results of chemical analysis of wines showed that all wine samples produced by fermentation with immobilized yeast cells had a slightly higher amount of alcohol, reducing sugars and total acidity, while specific mass, total and free SO₂ content were decreased using this method of fermentation. Furthermore, total biogenic amine content decreased by fermentation with immobilized yeast cells for both grape varieties. Wine produced from grape variety *Syrah* had higher content of biogenic amines compared to wine produced from *Merlot* grape. Histamine was the most abundant biogenic amine followed by 2-Phenylethylamine, while amount of Serotonine was the lowest.

Utjecaj dodatka tropa jabuke na svojstva kukuruznih snack proizvoda

Effect of apple pomace addition on properties of corn snack products

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Corn grits is a basic raw material for production of snack products, but recently various types of flours and dehydrated fruits and vegetables have been used to increase the nutritive value of these products. Apple pomace, as an inexpensive and primary by-product of apple juice and cider production, is a good source of dietary fibres, polyphenols and pectin. Because of that, the aim of this study was to investigate the effect of dehydrated apple pomace addition (5, 10 and 15%) on the properties of corn snack products.

Prepared samples with 15% of moisture content were extruded in the laboratory single screw extruder at temperature profile 135/170/170 °C, using a screw with compression ratio 4:1 and die with 4 mm diameter. Obtained extrudates were air-dried, and expansion ratio (ER), bulk density (BD), texture and colour were determined.

The results showed that the ER and fracturability of extrudates decreased, and BD increased with the addition of apple pomace. The hardness of extrudates increased with the addition of apple pomace, but not significantly for extrudates with 5 and 10% of apple pomace. The results for colour analysis indicated that extruded samples were darker and total colour change (ΔE) increased proportionally to the addition of apple pomace, with a more pronounced change in extruded samples.

**Utjecaj vremena i temperature miješanja na svojstva
djevičanskog maslinovog ulja sorte Levantinka**

**Influence of malaxation time and temperature on
"Levantinka" virgin olive oil properties**

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Ispitivan je utjecaj vremena i temperature miješanja u procesu proizvodnje na svojstva djevičanskog maslinovog ulja dobivenog iz sorte Levantinka. Miješanje maslinovog tijesta provedeno je pri temperaturama 26, 36, 46 °C. Pri svakoj navedenoj temperaturi ispitan je utjecaj vremena miješanja (30, 45, 60 min). U cilju procjene kvalitete dobivenih ulja provedena su ispitivanja slobodnih masnih kiselina (SMK), peroksidnog broja (PB), K-brojeva, sadržaja ukupnih fenola, organoleptičkih svojstava, oksidacijske stabilnosti ulja (Rancimat test) te održivosti ulja (DPPH test).

Na osnovu dobivenih rezultata može se zaključiti da i temperatura i vrijeme miješanja imaju utjecaja na svojstva i kvalitetu ulja. Najniži PB, najveći udjel ukupnih fenola te najbolja održivost ulja dobiveni su pri temperaturi od 36 °C i vremenu miješanja od 30 min. Najniži sadržaj SMK i najbolja oksidacijska stabilnost također su dobiveni pri istoj temperaturi (36 °C), ali nešto duljem vremenu miješanja (SMK 60 min, Rancimat test 45 min).

Vrijednosti K-brojeva su bile u granicama za djevičanska maslinova ulja za uzorke prerađene pri 26 °C i 36 °C u vremenu miješanja od 30 i 45 min. Senzorskom analizom najbolju ukupnu ocjenu su pokazali uzorci prerađeni pri istim uvjetima miješanja kao i kod K-brojeva, dok je gorčina bila najizraženija u uzorcima pri 36 °C i vremenu miješanja 30 min te pikantnost pri 36 °C i vremenu miješanja 60 min.

Antiradikalna aktivnost polifenolnih spojeva starih sorti jabuka

Antiradical activity of polyphenols from old apple varieties

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The aim of this work was to study the antiradical activity of polyphenolic compounds from old, ancient apple varieties grown in Croatia (*Crvenka*, *Pisanika*, *Ledenara*, *Adamova zvijezda*, *Slavonska srčika* and *Wild apple*). Polyphenolic compounds were extracted from apple peel (acidified methanol) and flesh (80% methanol) by using ultrasonic bath. The scavenging of synthetic, free DPPH radical by polyphenolic compounds was studied until the reaction reached the steady state. A biphasic reaction was observed between apple polyphenols and DPPH radicals, with "fast" and "slow" scavenging rate. The antiradical activity of the peel of apples *Pisanika*, *Ledenara*, *Crvenka*, *Adamova zvijezda* was similar and higher than antiradical activity of the peel of *Wild apple* and *Slavonska srčika*. On the other hand, antiradical activity of the flesh of *Wild apple* was significantly higher than antiradical activity of the flesh of other apples. The polyphenolic profile of wild apple showed that the compounds most likely to be responsible for a strong antiradical activity of apples are chlorogenic acids, phloretin derivatives, quercetin derivatives and flavanols. In conclusion, polyphenols of old apple varieties can be considered as strong free radical scavengers, especially wild apples. The overall results showed the need to preserve and protect these old varieties because they represent a significant source for horticultural biodiversity.

**Učinak nanočestica fullerena i fulenerola na inhibiciju
rasta plijesni *Aspergillus flavus***

**Effect of fullerene and fullerenol nanoparticles on
Aspergillus flavus growth inhibition**

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Although fullerenes and fullerenols have been reported to act as strong antimicrobial agents, recent reports of their effect on single cell eukaryotic microorganisms, such as *Saccharomyces cerevisiae*, indicate lack of antifungal activity. In order to fill a knowledge gap, we examined antifungal activity of stable aqueous fullerene nC₆₀ nanoparticles and fullerenol C₆₀(OH)₂₄ nanoparticles against *Aspergillus flavus*, one of the most important food contaminants.

Stable aqueous fullerene nC₆₀ and fullerenol C₆₀(OH)₂₄ nanoparticles were prepared according to Marković et al [1]. *A. flavus* mycelia have been grown on YES agar during 7 days at 28 °C according to Gandomi et al [2]. Lipid peroxidation products (TBARS) content in *A. flavus* mycelia was determined according to Luschchak and Gospodaryov [3].

The results revealed no effect of the nanoparticles added to the cultivation media at 10 and 100 ppb, respectively, over a 7-day growth period. Additionally, redox activity of fullerene and fullerenol nanoparticles was investigated by measurement of lipid peroxidation products (TBARS) in *A. flavus* mycelia. Fullerene and fullerenol nanoparticles had different effects on oxidative stress in the fungus. Whilst nC₆₀ nanoparticles showed slight pro-oxidant activity by increasing TBARS (p<0.05), C₆₀(OH)₂₄ nanoparticles exhibited antioxidant activity and reduced their formation.

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**Utjecaj mikrovalnog zagrijavanja na oksidacijsku stabilnost
ulja konoplje (*Cannabis sativa* L.)**

**The effect of microwave heating on the oxidative stability
of hemp (*Cannabis sativa* L.) oil**

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The aim of this paper was to study the influence of parameters of microwave heating (time, power) on the oxidative stability of cold pressed hemp (*Cannabis sativa* L.) oil. Furthermore, the influence of individual natural antioxidants (rosemary extract, green tea extract, pomegranate extract, share of 0.1%, 0.2%) and synthetic ones (PG, BHA, 0.01%) on the change of the oxidation stability of hemp oil were also examined. Oil samples were heated in a microwave oven at different power levels (180 W, 300 W, 450 W) for 5 minutes. The influence of microwave heating time (5, 10, 15, 20, 25 min) at constant power devices on the oxidation stability of hemp oil was investigated. The oxidative deterioration of oil is shown by the peroxide number. Increased power of microwave heating leads to temperature rising and higher oxidative deterioration of hemp oil. Longer oil treatment time with microwave heating shows the decrease in the oxidation stability of hemp oil. The addition of rosemary extract type OxyLess CS achieves greater stability of oil compared to the application of other antioxidants.

**Utjecaj mikorize i kvasaca na kakvoću vina
sorte Merlot (*Vitis vinifera* L.)**

**Influence of mycorrhizae and yeast strain on quality of wine
variety Merlot (*Vitis vinifera* L.)**

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Mikoriza je simbioza korjena vinove loze i micelija mikoriznih gljiva koja omogućuje biljci bolju apsorpciju hranjivih tvari iz tla, što se može u konačnici odraziti na kakvoću vina. Cilj istraživanja bio je usporediti kemijska i senzorska svojstva vina sorte Merlot (berba 2013.), u ovisnosti o naciepljivanju korjena mikorizom. Osim toga, fermentacija moštova je provedena pomoću dvaju različitih kvasaca: hibrida *Saccharomyces cerevisiae* pripremljenog za fermentaciju *bordoških* tipova crnih vina kao što je Cabernet sauvignon, te hibrida između *Saccharomyces cerevisiae* i *Saccharomyces paradoxus*. U vinima su određeni sljedećikemijski parametri: alkohol, ukupne kiseline, pH, ukupni suhi ekstrakt, reducirajući šećeri, ekstrakt bez šećera, pepeo, te ukupni i slobodni SO₂. Također su određeni ukupni antocijani pH diferencijalnom metodom, polifenoli mikro Folin-Ciocalteuovom metodom, antioksidativna aktivnost (ABTS metodom) te ton i gustoća boje. Senzorsko ocjenjivanje je provedeno metodom 100 bodova. Rezultati su pokazali značajan utjecaj kvasaca na udio polifenola, antocijana i antioksidativnu aktivnost, dok utjecaj mikorize nije pokazao značajan utjecaj na navedene parametre. Odsutnost utjecaja mikorize može se objasniti idealnim vremenskim uvjetima za zrenje grožđa u 2013. godini, tako da je grožđe sazrelo na lozi bez naciepljene mikorize imalo dovoljnu količinu hranjivih tvari.

Minerali u orašastim plodovima i sušenom voću određeni instrumentalnom tehnikom ICP-OES

Minerals in nut and dried fruits analyzed by instrumental technique ICP-OES

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Minerali zajedno s vitaminima čine skupinu zaštitnih nutritivnih tvari, neophodnih ljudskom organizmu. S obzirom na dnevne potrebe ljudskog organizma za mineralima razlikuju se makro i mikronutritivni minerali. U radu su analizirani makronutritivni minerali: Ca, K, Mg, Na i mikronutritivni: Cu, Fe, Mn i Zn. Obradeno je 5 uzoraka orašastih plodova (orah, brazilski orah, badem, lješnjak i pistacio) i 6 uzoraka sušenog voća (groždice, smokve, šljive, banane, papaja, brusnica). Uzorci su pripremljeni mikrovalnom digestijom uz HNO₃ i H₂O₂. Određivanje svih metala je obavljeno na instrumentu ICP-OES. Maseni udjeli određenih makronutritivnih minerala, na osnovu dobivenih rezultata, mogu se rasporediti u sljedeći opadajući niz Na > Mg > Ca > K. Najviše vrijednosti Na u orašastim plodovima su dokazane u uzorku pistacia (9113 µg/g), a najmanje u uzorku oraha (4.98 µg/g). Dok su kod sušenog voća najviše vrijednosti zabilježene za suhe smokve Na (2172 µg/g), a najniže za papaju (236 µg/g). U svim ispitivanim uzorcima orašastih plodova sadržaj Mg bio je veći od sadržaja Ca. Iz analizirane skupine mikronutritivnih minerala najveći sadržaj u svim ispitivanim uzorcima analiziran je za Fe. Visoki maseni udio Fe određen je u uzorcima badema 43,16 µg/g i suhih šljiva 59,89 µg/g. Sadržaj Zn u orašastim plodovima je vrlo sličan, u rasponu od 22,77 do 39,46 µg/g. Najviši udjel Zn utvrđen je u brazilskom orahu i iznosi 39,46 µg/g. Ukupni sadržaj svih analiziranih minerala u orašastim plodovima ukazuje na najviše vrijednosti za badem i brazilski orah. U uzorcima sušenog voća najviše vrijednosti makronutrijenata ima suha smokva, a visoke vrijednosti mikronutrijenata suha šljiva. Usporedbom dobivenih rezultata analiziranih elemenata u ovom radu s rezultatima iz literature može se uočiti da postoje određene varijacije u sadržajima svih određenih elemenata. Vjerojatno su posljedica različitog zemljopisnog porijekla ispitivanih uzoraka, različitih postupaka uzgajanja biljaka, različite sposobnosti biljaka u apsorpciji pojedinih elemenata kao i različitih postupaka prilikom prerade, pakovanja i transporta finalnog proizvoda.

Određivanje polifenolnih sastojaka crnih vina iz vinogorja Baranja

Determination of polyphenolic compounds in red wines from Baranja vineyard

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In this study, bioactive polyphenolic compounds from red wines were investigated. For the characterization of individual polyphenolic compounds belonging to phenolic acid and flavanol class, easy and reliable high performance liquid chromatography method with photodiode array detection was developed. Total polyphenols and total flavonoids were also investigated by using simple spectrophotometric methods. All methods were checked for their linearity, limit of detection, limit of quantification, precision and accuracy. Developed and validated procedures were applied for the determination of polyphenolic compounds in two wines from Baranja vineyards, Croatia. The most abundant compounds found in red wines were gallic acid and (+)-catechin followed by caffeic acid, *p*-coumaric acid, (-)-epicatechin. The developed methods were shown to be precise and accurate for the determination of polyphenolic compounds from red wines.

Mjerenje i regulacija razine pomoću ultrazvučnog mjernog pretvornika i Arduino mikroupravljača

Measurement and level regulation with ultrasound sensor and Arduino microcontroller

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Arduino open-source microcontroller platform has been proved as a modular and cheap platform for a vast number of different tasks and applications. Strong community and potent hardware base with a large number of sensors and actuators that are premade for Arduino platform (called shields) have made this possible. The aim of this work was to assess the feasibility of HC-SR04 ultrasound sensors with Arduino Uno R3 platform and relay shield as a solution for real world application of level regulation. A model system is investigated, comprised of a liquid tank, one HC-SR04 ultrasound sensor, Arduino Uno R3 microcontroller board and relay shield with two solenoid valves. Custom software was developed with the aid of open source libraries and tools for implementing control algorithms. With Arduino support for serial communication, communication and control is very easy by means of personal computer appropriate application, with graphical user interface. Further, Arduino Uno R3 with low price is very competitive to dedicated and established solutions for process automation such as programmable logic controllers in small family enterprises.

Utjecaj fenolnih spojeva iz ljekovitog bilja na antocijanski profil i svojstva boje ekstrakata grožđa

Anthocyanins and color profiles of grape extracts enriched with phenolics of medical plants

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Anthocyanins possess great potential for utilization as natural food colorants and nutraceuticals due to their attractive colors and documented health benefits. The stability of anthocyanins depends on a combination of several factors, including their structure and concentration, pH, temperature, light intensity, the presence of metal ions, oxygen, ascorbic acid, sugar and their degradation products. The addition of phenols to anthocyanin solutions has stabilizing effect on anthocyanins during processing and storage.

The objective of this study was to investigate the anthocyanins and color profiles of extracts prepared from grape skins, pressed grapes and grape pomace, which were enriched with phenolics from medical plants, after the exposure to different light conditions. The extraction of anthocyanins was performed using mixture of methanol and water (60:40) acidified with 1% (w/v) HCl. Phenolics from peppermint (*Mentha piperita* L.), immortelle (*Helichrysum arenarium* L.), or wild thyme (*Thymus serpyllum* L.) were added (0.4%) to the extracts. The samples were stored at +21 °C under daylight, fluorescent light and dark, and at +8 °C in dark, for 100 days. The correlations between contents of copigmented, monomeric, polymeric and total anthocyanins, and the color characteristics (proportions of red, yellow and blue color, color intensity, and hue) were established through spectrophotometric measurements.

Procjena izabranih citolitičkih i proteolitičkih parametara slada

Evaluation of selected cytolytic and proteolytic parameters of malt

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Quality of malt depends on the quality of barley. Therefore, its evaluation is very important for breeders, growers and producers of malt and beer.

Barley malt analytics is based on describing the three modification procedures of malted barley grain - cytolysis, proteolysis and amylolysis. Parameters which determine level of cytolytic modification are friability, β -glucans and viscosity of the congress wort. The Kolbach index is a parameter generally used for the evaluation of proteolysis. Information about the activity of proteolytic and cytolytic enzymes can also be measured by relative extract at 45 °C.

In this study, four selected cytolytic and proteolytic parameters of the malt were evaluated – friability, β -glucans in wort, Kolbach index and relative extract at 45 °C. The malt samples were prepared by a standard micromalting method from 5 varieties of spring barley grown over the years 2009-2011 in three different agricultural production areas of Slovak Republic. The aim of our study was to determine which of the malt parameters depends on the variety of barley used to make the malt, growing location and year. Results of our work did not show statistically significant effect of the variety and the growing location on the malt friability, but highly significant influence ($P < 0.01$) of the year on malt friability was confirmed.

Parameter β -glucans in the wort was affected by all sources of variability and the strongest influence was detected by the variety and the year of growth of malting barley.

The Kolbach index was strongly ($P < 0.01$) affected by the year and it also showed significant difference considering the location. Barley variety did not have significant effect on the Kolbach index.

The relative extract at 45 °C was influenced by all of the stated effects, but barley variety had the most significant influence ($P < 0.01$) on this parameter.

Based on the results of our work, we can state that β -glucan in wort and relative extract at 45 °C were parameters fixed by the variety. We can conclude that friability and Kolbach index were significantly affected by the year.

**Utjecaj dodatka pogače od konoplje i pšeničnih klica
na kakvoću tjestenine**

**Influence of the addition of deffated hemp cake
and wheat germ on pasta quality**

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The high nutritional value of hempseed is well characterised and includes phytochemicals, vitamins (A, C and E) and minerals. Defatted hemp or hemp cake (a by-product of crushing hempseeds for oils) is high in protein and low in oil. In the wheat grain, most nutrients, with the exception of starch, are concentrated in germ but most of them are generally used in animal feed formulations, which is why the precious wheatgerm source has not been amply, rationally, and efficiently utilized. The germ provides three times as much protein, seven times as much fat, fifteen times as much sugars and six times as much mineral content than wheat flour. Influence of the addition of deffated hemp cake (DFHC) (5 and 10%) and wheat germ (WG) (10, 20 and 30 %) on quality of durum pasta was investigated. Pasta was produced on laboratory mini press (moisture content of mixtures was set to 36%, mixing time was 10 min) and air dried at room temperature. Evaluation of uncooked and cooked pasta samples was performed (determination of colour, optimum cooking time, water absorption and texture profile analysis).

Stanje i mogućnosti proizvodnje mlijeka u Požeško-slavonskoj županiji

Condition and possibility of milk production in Požega-Slavonia County

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Mlijeko je biološka tekućina, karakteristične boje, mirisa i okusa, koju izlučuju mliječne žlijezde ženki sisavaca ili žene [1].

Pod pojmom mlijeko, uvijek se podrazumijeva „kravlje mlijeko“, za sve ostale vrste mlijeka mora biti istaknuto od koje životinje potječe, kao npr. „ovčje mlijeko“, „kozje mlijeko“, „bivolje mlijeko“ ili neka druga vrsta mlijeka. Posebno se deklarira „majčino mlijeko“, koje se normalno ne pojavljuje na tržištu, ali zauzima važno mjesto u nutricionističkim i medicinskim istraživanjima [1].

Sve vrste mlijeka sadrže gotovo iste sastojke, ali u različitom udjelima.

Mlijeko sadrži nekoliko stotina hranjivih tvari. Zato je u prehrambenom smislu mlijeko nezamjenjiva namirnica. Proizvodnja mlijeka i mliječnih proizvoda za svaku zemlju je strateško pitanje i ona je odraz uređenosti prehrambene proizvodnje u nekoj zemlji.

Budući da Hrvatska ne zadovoljava svoje potrebe u proizvodnji mlijeka (prosječno 40% potrošnje uvozi), ovdje smo prikazali trenutnu proizvodnju mlijeka, u odnosu na prije devet godina i mogućnosti povećanja proizvodnje mlijeka u Požeško-slavonskoj županiji te djelu Brodsko-posavske županije, odnosno pedeset kilometara u polumjeru od Požege.

U Požegi se nalazi mljekara sa mogućnošću prerade 100 000 L dnevno mlijeka, a trenutačno nema vlastitog otkupa mlijeka.

U radu smo prikazali mogućnosti povećanja proizvodnje s obzirom na infrastrukturu i raspoložive obradive površine zemlje (oranice i vrtovi, livade), koji bi trebali biti u funkciji podizanja stočarske proizvodnje.

[1] Lj. Tratnik, *Mlijeko –tehnologija, biokemija i mikrobiologija*, Hrvatska mljekarska udruga, Zagreb, (1998) 13-16.

**Povezanost izabranih fizikalno-kemijskih karakteristika i vremena
skladištenja meda**

**Relationship of the selected physicochemical characteristics
and honey storage duration**

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Product durability is defined in the regulations as the date (date of minimum durability), to which the food retains its specific properties, if stored properly. As a product with high sugar content and low water activity, honey is microbiologically stable, but susceptible to physical and chemical changes resulting in darkening, taste and aroma loss. The main focus of this study was to determine parameters prescribed by the regulations, hydroxymethylfurfural (HMF) content and diastase activity (DN), both influenced by the length and the storage conditions. Additionally, the activity of glucose-oxidase, an enzyme related to the antimicrobial activity of honey, and color (by Lovibond Honey ColorPod and spectrophotometric method) were determined. Four types of honey were analysed: chestnut (*Castanea sativa* Mill.), sage (*Salvia officinalis* L.), black locust (*Robinia pseudoacacia* L.) and honeydew honey. The samples were stored at the room temperature, in the dark, and when analysed, black locust and honeydew honey samples were 4.5, while sage and chestnut honey were 5.5 years old. The results showed significant differences of the monitored parameters according to the honey type and within the same honey samples, especially in chestnut honey. Unlike black locust and sage honey, all of the honeydew honey samples and some chestnut honey samples, after a long-term storage, met the prescribed requirements.

Određivanje teksture (čvrstoće) i SFC profila binarnih i ternarnih smjesa palminog ulja, palminog stearina i sojinog ulja

Determination of texture (hardness) and SFC profile of binary and ternary mixtures of palm oil, palm stearin and soybean oil

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U ovom radu proučavani su sadržaji čvrstih triglicerida (SFC) pomoću nuklearne magnetske rezonance i tekstura (čvrstoća) binarnih i ternarnih smjesa palminog ulja (PO), palminog stearina (PS) i sojinog ulja (SO). Reološka svojstva teksture, odnosno čvrstoće ovih smjesa određena su penetracijom pri konstantnoj brzini. Pripremljene su binarne smjese PO/SO, PS/SO, PO/PS i ternarne smjese PS/PO/SO s 20%tnim povećanjem udjela svake pojedine komponente. Statički su kristalizirane u hladnjaku na -25 °C kroz 20 minuta, a zatim temperirane kroz 48 sati na 15 °C. S obzirom da se ovi lipidni sistemi uobičajeno koriste u proizvodnji margarina i masti, cilj rada bio je procijeniti fizikalne karakteristike kao što su tekstura (čvrstoća) i SFC profil, te njihove međusobne odnose. Dobiveni rezultati ukazuju da se povećanjem čvrste komponente (PO i PS) u smjesama PO/SO i PS/SO povećavala čvrstoća kao i SFC vrijednost. Slični rezultati dobiveni su i kod proučavanih ternarnih smjesa. Izuzetak je smjesa PS/PO sa više od 50% PS gdje porastom SFC vrijednosti nije došlo i do očekivanog porasta čvrstoće.

Navike konzumiranja kavovina unutar studentske populacije

Habit of consuming coffee substitutes within the student population

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Studentska populacija je zdravstveno ugrožena skupina koja uz nedostatak vremena poseže za "trendovskom hranom". Tijekom tog životnog razdoblja događaju se brojne tjelesne i psihičke promjene. Adolescenti postaju svjesni da načinom prehrane mogu utjecati na izgled tijela i nerijetko počinju eksperimentirati s hranom. U radu se opisuje utjecaj načina života i prehrane na zdravlje. Cilj rada bio je istražiti stavove prema značenju prehrambenih navika na zdravlje studenata, te istražiti upoznatost studentske populacije i učestalost konzumiranja kavovina. Kao instrument istraživanja je korišten anketni upitnik sačinjen od pitanja i tvrdnji koje su ispitanici ocjenjivali ocjenama od 1 do 5. Analizom prehrambenih navika studenata utvrđeno je da se neke izuzetno nutritivno bogate namirnice više ne konzumiraju, a to su surogati kave tzv. kavovine. Nutritivni sastav kavovina sve je osim zanemariv, a danas ih konzumiraju ljudi koji su osviješteni koliko je prehrana bitna za zdravlje. U povijesti kavovine su poznate kao izrazito zdrava hrana, dragocjena u prehrani rekreativaca, sportaša i mladeži u razvoju. Istraživanje ukazuje na promjenu prehrambenih i životnih navika studenata. Edukacija o uravnoteženoj prehrani može poboljšati zdravstveno stanje čime su postignuti preduvjeti za prevenciju kroničnih i degenerativnih bolesti.

**Antimikrobna aktivnost esencijalnih ulja majčine dušice iz Pelisterske regije
(Bitola, Makedonija) kao mogući prirodni izvor konzerviranja hrane**

**Antimicrobial activity of essential oil from *Thymus tosevii* Vel. subsp.
tosevii var. *degenii* (Lamiaceae) from Pelister (Bitola, Macedonia)
as a potential natural food preservative**

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The aim of this study was to investigate whether essential oil of the plant *Thymus tosevii* Vel. subsp. *tosevii* var. *degenii* (Lamiaceae), endemic species in Pelister (Baba Mountain, Bitola, Macedonia) manifest antibacterial activity against *Salmonella enteritidis*, *Escherichia coli* and *Bacillus subtilis*, as well as antifungal activity against *Aspergillus niger* and anti-yeast activity against *Candida albicans*. Apart from this, preliminary investigations were made to determine antibacterial activity of this essential oil against *Staphylococcus aureus*, *Enterococcus faecalis* and *Proteus mirabilis*.

The essential oil was obtained from the aerial parts at flowering stage by hydro-distillation. Unger apparatus was used to obtain plant's essential oil. Antimicrobial activities of the essential oil were evaluated by a disc diffusion method.

Essential oil from the plant *Thymus tosevii* Vel. subsp. *tosevii* var. *degenii* (thyme) showed different antimicrobial activity against tested microorganisms, depending on the concentration of essential oil used, as well as the type of microorganism.

The most sensitive microorganisms to the effect of *Thymus tosevii* Vel. subsp. *tosevii* var. *degenii* essential oil were *Salmonella enteritidis* and *Escherichia coli*, moderately susceptible were *Candida albicans* and *Bacillus subtilis*, and the less sensitive microorganism was *Aspergillus niger*. The essential oil of *Thymus tosevii* Vel. subsp. *tosevii* var. *degenii* manifested very weak antimicrobial activity against *Staphylococcus aureus*, *Enterococcus faecalis* and *Proteus mirabilis*.

**Procesna jedinica za fermentaciju i konstrukciona rješenja
fermentatora u Pivari Tuzla d.d.**

**Process units for fermentation and constructive solutions
of fermenters at Pivara Tuzla d.d. brewing company**

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A prime goal of process modernization in beer production is the simplification of mechanization and process control of exploitative process units. Traditionally, beer fermentation storage and maturation took place in underground vessels. After a short period of time Combi storage vessels were used, with cooling mantles incorporated. Those vessels were also a fermentation vessels. Modern technologies in beer production use cylindroconical tanks (fermenters). Usage of large tanks started a short period of time after, that could accept worth for one day production. The flat bottom of those tanks caused difficulties with yeast removal from such tanks and increased manual work. That is also a characteristic of Mind vessels. 10 – 15% inclination of vessel bottom did not increase efficiency. A desirable succes has been reached with cylindroconical tank (fermenter) adaption for main and additional fermentation, as well as asolution of problems related to CO₂, with continuous improvements made in recent years.

**Utjecaj roka berbe na primarne metabolite u grožđu sorte
Plavac mali (*Vitis vinifera* L.)**

**Influence of harvest date on the primary metabolites of
Plavac mali (*Vitis vinifera* L.) grapes**

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The taste, the sensation, the odor, the color of wine are the results of a complex interaction of a multitude of compounds primarily synthesized in grapes during ripening. "Plavac mali" is known as a variety that can have green, blue and almost dried berries in the same bunch at the same time. It is believed that green contributes to increasing acidity. We investigated changes in the composition and the content of organic acids (malic, tartaric and citric), total acidity, pH, potassium and sugar components (glucose and fructose) in the grape variety "Plavac mali" during four different harvest dates in central and northern Dalmatia. The green berries were found only at the first harvest date at both locations. The determination of organic acids was carried out using high performance liquid chromatography HPLC-DAD and the determination of individual sugars was carried out using an enzymatic assay kit on the UV-Vis spectrophotometer. Significant differences were found between the four harvest dates in both observed locations as well as in the content of certain primary metabolites observed between the two locations. The sugar content increased with the maturation and it reached the values of 75.67 °Oe to 93.83 °Oe in central Dalmatia, and 69 °Oe to 84.67 °Oe in the northern. On the last harvest date, the ratio of glucose and fructose in grape berries was almost equal, 108.20 g/kg and 105.83 g/kg respectively in terms of central Dalmatia and 111.73 g/kg and 94.05 g/kg, respectively in terms of northern Dalmatia. The content of malic acid declines during maturity in central Dalmatia from 2.17 g/L to 0.25 g/L, and in the conditions of northern Dalmatia from 3.43 g/L to 0 g/L. The changes in the content of tartaric acid in both locations were less evident.

Neke značajke kvalitete trupova i mesa križanaca svinja

Some carcass and meat quality traits of pig crossbreeds

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Meat quality in pigs depends on genetic and non-genetic factors and certainly breed has a big part in the carcass yield. The biggest indicator of the quality of pork is the participation of the highest quality parts (pork leg and boneless).

We evaluated the carcass and meat quality traits of the native crossbreeds Large White and Swedish Landrace. Eleven pigs (half castrated males and half females) were reared and slaughtered at a predetermined slaughter age. The average body mass prior to slaughtering amounted to 107.8 kg. Dressing percentage was found at 68.51%. Cold carcass weight after 24 hours refrigeration was 33.78 kg. Meat quality parameters showed the highest intramuscular fat content (6.04%). The share of top quality meat categories in crossbreeds in the total mass of carcasses was 40.78%.

Utjecaj sorte i vinogorja na antioksidacijsku aktivnost, te sadržaj polifenola i antocijana u crnim vinima

Influence of variety and vineyard on antioxidant activity, polyphenols and anthocyanins content in red wines

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Anthocyanins play a crucial role in the color of red wine; however they contribute little to the taste of wine. Anthocyanins developed in the leaves of photosynthetic plants as a protection from the photo-damage of UV and blue-green light. These pigment molecules are effective sunprotectors for grapes. In addition to their primary function, they also act as antioxidants, protecting free radical oxidation. This paper deals with the influence of vineyard and variety on antioxidant activity, flavonoids, polyphenols and antocyanins content in red wines. The samples of red wines were produced in vineyards of continental Croatia (*Merlot, Frankovka, Pinot noir, Cabernet Sauvignon* and *Zweigelt*) and coastal Croatia (*Plavac mali, Teran, Merlot* and *Babić*). It was found that variety, vineyard position and climatic conditions had influence on flavonoids, polyphenols and antocyanins content in red wines.

The results of analysed wines showed that coastal Croatian wines had higher content of polyphenols and flavonoids than continental Croatian wines. There was no significant difference between antioxidant activity of continental and coastal Croatian wines. The wine of coastal Croatia vineyards, such as variety *Teran*, had the highest content of anthocyanins compared to all the examined wines.

Sastav topljivih saharida zrna soje s obzirom na uvjete uzgoja

Composition of soluble saccharides in soybean grain with regard to growing conditions

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Soybeans have long been recognized not only as a valuable source of edible oil but also as an excellent source of protein for feeding both animals and humans. The feed value of soybean, however, is limited by the oligosaccharides because of flatulence based on their indigestibility. As oligosaccharides act as a substrate for intestinal bacteria, they are also considered as prebiotics. The objective of this study was to evaluate the composition of soluble saccharides (monosaccharides, disaccharides and oligosaccharides) of four soybean genotypes created at the Agricultural institute Osijek as influenced by irrigation and nitrogen fertilization. Soybean samples were ground and soluble saccharides were extracted with water and separated by high performance liquid chromatography. Saccharides were identified by their retention time and quantified by peak area using external standard procedure. The analysis of variance showed significant effect ($p \geq 0.05$) of genotype and irrigation on concentration of stachyose, raffinose, sucrose, fructose and total oligosaccharides. The interaction between genotype, irrigation and nitrogen fertilization also revealed a significant effect ($p \geq 0.05$) on these grain compositions. Among the sugars studied, the highest content in soybean was sucrose, which was 46.64% of total saccharides (mean of all treatments). Oligosaccharides are represented with 45.48% of the total saccharides, with 32.03% percentage of stachyose and 13.45% percentage of raffinose. From monosaccharides in soybean grain, low concentration of glucose, galactose and fructose was also found.

**Utjecaj temperature i vremena sušenja na udio ekstrahiranih
fenolnih tvari iz tropa grožđa sorte "Portogizac"**

**Influence of temperature and drying duration on extraction yield
of phenolic compounds from grape pomace variety "Portogizac"**

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The aim of this work was to investigate the influence of drying temperatures and duration of drying on extraction yield of phenolic compounds (total phenolic compounds, TPC; total extractable proanthocyanidins, TPA; total flavonoids, TF), as well as on antioxidant activity (AA) of grape pomace extracts. Drying was performed in a fluidized bed drier at different temperatures (60 °C, 70 °C and 80 °C) for 90 min, 135 min and 180 min. Extractions of phenolic compounds were performed from undried and dried grape pomace at 80 °C using 50% of aqueous ethanol solution for 120 min. Grape pomace extracts were analysed spectrophotometrically using Folin-Ciocalteu micro-method at 765 nm [1], method based on acid hydrolysis and formation of red colour at 540 nm [2] and the aluminium chloride colorimetric assay at 510 nm [3], for TPC, TPA and TF, respectively. AA of extract were evaluated by spectrophotometric method at 515 nm against stable 2,2 diphenyl-1-picrylhydrazyl radical (DPPH•) [4].

Contents of phenolic compounds and antioxidant activity of extracts obtained from undried grape pomace were 73.83 mg_{GAE}/g_{db}, 30.53 mg/g_{db}, 42.24 mg_{CE}/g_{db}, and 0.35 g_{inhDPPH}/g_{db} for TPC, TPA, TF and AA, respectively. Drying temperature and time influenced the content of phenolic compounds and the results for extracts obtained from dried grape pomace compounds were lower, up to 13.2 %, 43.1 %, 15.3 % and 21.0 % for TPC, TPA, TF and AA, respectively.

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Nutritivna vrijednost masti kozjeg mlijeka

Nutritive value of goat milk fat

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In recent years there has been an increased interest for fatty acid composition of goat milk. The aim of this study was to analyze the fatty acid composition of goat milk compared to cow milk.

Milk samples were taken from dairy goats (n=20) grazing on pastures, and from dairy cows (n=20) fed with concentrate, grass hay and premix. Fatty acid profile was analyzed by gas chromatography, using Hewlett Packard 5890 series II gas chromatograph with flame ionization detector, and capillary column HP88 (60m x 0.250mm x 0.20µm). The obtained results showed that goat milk contained higher content of butyric (C4:0), caproic (C6:0), caprylic (C8:0), capric (C10:0), lauric (C12:0), myristic (C14:0), palmitic (C16:0) and linoleic acid (C18:2), but lower content of stearic (C18:0) and oleic acid (C18:1) than cow milk. This specific fatty acid composition contributes to easier digestion of goat milk fat and add significantly to its nutritive value.

Komparativna analiza sastava kravljeg i ovčjeg sira

Comparative analysis of composition of cow and sheep cheese

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Cheese is nutritious food made mostly from the milk of cows, but also from other mammals, including sheep, goats, buffalo, reindeer, camels, yaks etc. The aim of this work was to analyze the differences in chemical composition between traditional cow's and sheep's cheese. Cheese samples were taken from the same dairy producer from Macedonia. They were analyzed for moisture content, fat content, protein content, content of NaCl, content of dry matter and fat content in dry matter, using standard chemical methods.

According to the obtained results, sheep cheese samples contained more fat (21.15%), and more protein (39.65%), but less carbohydrates (15%) than cow cheese samples. The difference in the chemical composition between cow's and sheep's cheese is a result of different chemical composition of cow's and sheep's milk, which causes differences in their nutritive values.

Procjena rizika od prehrambenih aditiva u RH

Risk assessment of food additives in Croatia

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Prehrambeni aditivi se uobičajeno koriste u suvremenoj proizvodnji hrane zbog tehnoloških potreba. Toksikološki su evaluirani i dozvoljeni za uporabu, ali stvaran unos tijekom određene prehrane može utjecati na prekoračenje prihvatljivog dnevnog unosa (engl. Acceptable Daily Intake –ADI) . Istraživanje koje je provela Hrvatska agencija za hranu u razdoblju 2010. – 2012. imalo je za cilj ustanoviti stvarnu izloženost potrošača u RH prehrambenim aditivima iz hrane te na temelju izračuna putem procijenjenog dnevnog unosa, u odnosu na prihvatljivi dnevni unos izraziti potencijalni rizik za potrošače. Istraživanje su zajednički realizirali Hrvatski zavod za javno zdravstvo te Zavod za javno zdravstvo „Dr. Andrija Štampar“, a provedeno je kroz tri faze. Prva faza uključivala je ispitivanje prehrambenih navika potrošača vezano uz unos prehrambenih aditiva iz hrane, a što je bilo potrebno za drugu fazu prilikom koje se provelo analitičko ispitivanje određenih vrsta hrane koje su se pokazale kao najčešće konzumirane. Treća faza odnosila se na matematički izračun, odnosno izračun između procijenjenog i preporučenog dnevnog unosa aditiva iz hrane.

Zaključeno je kako je najveća učestalost konzumiranja hrane iz grupa hrane koje sadrže aditive iz grupe masti i ulja te konditorski proizvodi – gume za žvakanje. Rezultati sigurnosne procjene aditiva u Republici Hrvatskoj ukazuju da skoro svi aditivi (36 od 38) pripadaju prvoj (16 od 38) i drugoj (20 od 38) sigurnosnoj skupini u kojima je utvrđeni unos aditiva daleko ispod razine ADI, a samo dva aditiva (konzervansa) pripadaju trećoj skupini (E 249 i E 250). Stoga je i dana preporuka o daljnjem monitoringu i praćenju aditiva iz treće sigurnosne skupine, dok se vezano za ostale vrste aditiva, bez obzira što pridaju u prve dvije skupine dala preporuka o pravilnoj i izbalansiranoj prehrani.

Analiza baranjske začinske paprike

Analysis of Baranya spice pepper

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Paprika (*Capsicum annum* L.) je jedna od najznačajnijih povrćarskih kultura u svijetu i kod nas. Također, postoji veliki broj sorti začinske paprike koje se razlikuju po boji, obliku, veličini, aromi te stupnju ljutine. Plod paprike se prvenstveno konzumira kao svježe povrće ili osušen kao začim, ali je opseg primjene vrlo širok (prehrambena, farmaceutska, kozmetička industrija). Začinska paprika se koristi za proizvodnju mljevene začinske paprike i oleorizina. Najvažnije osobine i svojstva mljevene začinske paprike se indirektno ocjenjuju prema sadržaju karotenoida, kapsaicina, fenola, vitamina i antioksidativnoj aktivnosti. Na hrvatskom tržištu se trenutno mogu naći različiti gotovi proizvodi mljevene začinske paprike. Međutim, ti proizvodi su nestandardizirani i bez geografskog podrijetla. Cilj ovog istraživanja bio je analizirati i standardizirati hrvatsku začinsku papriku "Baranjka" kako bi se doprinijelo prepoznatljivosti proizvoda te osigurala konkurentnost proizvodnje začinske paprike za potrebe prehrambene i farmaceutske industrije. Standardizacija začinske paprike će također olakšati brendiranje i ulazak na tržište zaštićenih proizvoda s kontroliranim geografskim podrijetlom s područja kontinentalne Hrvatske čiji je neizostavni sastojak začinska paprika. Istraživanje je provedeno prikupljanjem i analiziranjem većeg broja uzoraka mljevene začinske paprike proizvedene tijekom 2012. i 2013. godine na obiteljskim poljoprivrednim gospodarstvima u Baranji koji svoj proizvod ujedinjuju u registrirani komercijalni proizvod pod nazivom "Baranjka". Tijekom laboratorijskih istraživanja provedene su analize začinske paprike na sadržaj kapsaicina, dihidrokapsaicina, ukupnih fenola, ukupnih flavonoida te je određena ukupna antioksidativna vrijednost. Sadržaj kapsaicina i dihidrokapsaicina su određeni primjenom tekućinske kromatografije visoke preciznosti (HPLC), a sadržaj fenola i flavonoida te ukupna antioksidativna aktivnost su određeni spektrofotometrijski. Analizom svih pokazatelja kvalitete začinske paprike utvrđeno je da lokacija i proizvodna tehnologija značajno utječu na iste. Sadržaj fenola u uzorcima začinske paprike značajno je varirao u rasponu od 160 do 230 mg GAE na 100 g paprike. Sadržaj flavonoida je također značajno varirao između uzoraka i to više nego sadržaj fenola te se kretao u rasponu od 150 do 360 mg kvercetina na 100 g paprike. Najveće varijacije među uzorcima paprike zabilježene su za antioksidativnu aktivnost čije su vrijednosti iznosile od 1850 do 8430 µM TEAC na 100 g paprike. Općenito, uzroci ljute paprike su pokazali višu antioksidativnu aktivnost što ukazuje na pozitivnu korelaciju s povećanim sadržajem kapsaicina i dihidrokapsaicina čiji je ukupan sadržaj bio izražen u SHV jedinicama (Scoville Heat Value) koje označavaju stupanj ljutine začinske paprike. Uzorci paprike su se vrlo značajno razlikovali prema SHV vrijednosti i to u rasponu od 919,9 do 7145,6. Na kraju, za lakše standardiziranje proizvoda i njegovu prepoznatljivost bit će potrebno ujednačiti tehnologiju proizvodnje začinske paprike kod svih proizvođača te utvrditi specifičnosti proizvodne lokacije.

Ispitivanje sadržaja histamina u alkoholnom i bezalkoholnom svijetlom pivu

The histamine content testing in alcoholic and non-alcoholic bright beer

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Food hypersensitivity is common. Its symptoms can occur when the consuming only few ppm of certain food substance. One of potential hypersensitive ingredient in beer is histamine. The aim of this research was to define methodology and determine presence and quantity of histamine in alcoholic and non-alcoholic bright beer and beer produced by biological and physical process.

HPLC analysis was performed with detection and quantification of histamine on absorption PDA detector set at 280 nm, after derivatisation with diethyletoxymethylenemalonate (DEEMM). Separation was performed at 16 °C on Zorbax XDB C18 (150 mm × 4.6 mm; 3.5 µm) with two mobile phases (A: acetate buffer 25 mM pH 5.8 with 0.02% sodium azide; B: acetonitril:methanol 80:20) and flow of 1mL/min in gradient elution mode.

Histamine content in alcoholic bright beers was between 0.085 mg/L and 0.119 mg/mL, whereas non-alcoholic beer contained 0.088 - 0.112 mg/L of histamine. Histamine content wasn't statistically different between alcoholic and non-alcoholic beer, as well as between biologically and physically produced beers.

Amounts of *n*-3 and *n*-6 fatty acids, fatty acids' profile and nutritive value of canned sardines in different coating media

Sastav masnih kiselina i nutritivna vrijednost konzerviranih sardina u različitim tekućim medijima

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Fish and fish products, especially fatty fish such as sardines, are a natural source of high-quality protein and essential fatty acids in human diet. Fish lipids contain long-chain *n*-3 polyunsaturated fatty acids (*n*-3 PUFA), of which eicosapentaenoic (EPA, 20:5*n*-3) and docosahexaenoic acid (DHA, 22:6*n*-3) play a vital role in human nutrition and health promotion. Among other, these fatty acids have positive cardio-protective effects. During canning process, sterilization step assures the safety of the product and it is adjusted to different coating media of the product. However, during high temperature treatment (>115 °C) changes of nutritive composition, especially fatty acid composition, can be substantial.

Fatty acid content, with emphasis on amounts of *n*-3 and *n*-6, and nutritional quality (atherogenic and thrombogenic index) of nine commercially available canned sardine products with different coating media (spicy vegetable sauce, sunflower oil, vegetable, tomato sauce, sunflower oil with lemon, olive oil, vegetable sauce, oil with chili peppers and escabeche sauce), all produced in Croatia, were investigated. Fatty acids were determined by a capillary gas chromatography using flame ionization detection. The lipid content of different products ranged from 12.88 to 34.05%. The fatty acids composition of nine canned sardine products contained 15.20-25.97% saturated (SFA), 25.10-70.08% monounsaturated (MUFAs) and 10.35-51.49% polyunsaturated acids (PUFAs). The main saturated and unsaturated fatty acids were C16:0 and C18:2(*n*-6) in all the investigated sardine products with the difference of canned sardine in olive oil characterized by prevalence of C18:1(*n*-9) fatty acid. The proportions of *n*-3 PUFAs of investigated canned products (ranged from 0.25% to 14.52%) were lower than *n*-6 PUFAs (ranged from 5.76% to 50.96%). The dominant PUFAs (*n*-3) were EPA C20:5(*n*-3) and DHA C22:6(*n*-3), and the highest levels were found in sardines in tomato sauce (0.54 g EPA and 1.29g DHA/100g edible portion). The AI (0.12-0.33) and TI (0.27-0.40) indices were in agreement with literature recommendations. Considering the recommended daily intake of *n*-3 PUFAs is 0.45 g per day for a healthy adult, in a single 125 g canned sardine the amount of PUFAs (*n*-3) ranges from 0.21 to 2.45 g, depending on the coating media. If fresh sardines are not available, canned products are, from a nutritional point of view, recommended to be consumed.

**Proizvodna iskorištenja i senzorno ocjenjivanje rakija proizvedenih od
prevrele komine grožđa cv. Graševina bijela**

**Production yields and sensory assessment of brandy produced
from fermented grape cv. Graševina white**

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Istraživanja su provedena na rakiji proizvedenoj od komine grožđa cv. Graševina bijela iz vinogorja Kutjevo. Istraživanja su trajala dvije godine i obuhvatila su berbe 2004. i 2005. godine. U pokusu je korištena komina dobivena na opremi za preradu grožđa tvrtke Kutjevo d.d., kao i na opremi obiteljskog gospodarstva Jakobović. Pokusna je rakija proizvedena u objektu Veleučilišta u Požegi. U 2004. godini pokus je proveden s kominom dobivenom nakon prešanja masulja (komina K) i postavljen je u šest varijanti uz tri ponavljanja (vrenje komine uz epifitnu mikrofloru, vrenje komine uz dodatak kvasca *Uvaferm CM*, dodatak preparata *Lallemand EX*, dodatak preparata *Lallzyme Cuvee Blanc*, dodatak preparata *Ultrazym 100G*, dodatak vinske kiseline). U 2005. godini su provedene dvije serije pokusa (komina dobivena nakon prešanja masulja (serija K), i komina zaostala nakon odvajanja samotoka (serija J)). Te je godine, uz dvije osnovne varijante (vrenje komine uz epifitnu mikrofloru, vrenje komine uz dodatak kvasca *Uvaferm CM*), ponovljen i pokus tretiranja komine jednim od primijenjenih preparata pektolitičkih enzima (dodatak preparata *Lallemand EX*). Pokusi su pod jednakim uvjetima izvedeni za svaku vrstu komine u 3 varijante i 3 ponavljanja. Proizvodna su iskorištenja rakija dobivenih u ovom pokusu bila niska sukladno niskoj razini šećera u grožđu i visokom stupnju iscijeđenosti komine. Senzorno je ispitivanje ukazalo da su sve pokusne rakije bile dobre kakvoće. Višu su ocjenu dobile rakije iz 2005. godine. Najbolje je ocjenjena rakija bila ona iz 2005. godine dobivena od neprešane komine (serija J) prevrele uz epifitne kvasce. Rakije dobivene od komine tretirane pektolitičkim enzimima i vinskom kiselinom nisu se značajno razlikovale po rangiranoj kakvoći od kontrolnih rakija.

Sekcija: Medicinska biokemija i farmacija
Topic: Medical biochemistry and pharmacy

2D i 3D molekulsko modeliranje derivata benzimidazola kao inhibitora dipeptidil-peptidaze III

2D and 3D molecular modelling of benzimidazole derivatives as dipeptidyl peptidase III inhibitors

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A molecular modelling study was performed on a series of benzimidazo-based inhibitors of human dipeptidyl peptidase III (DPP III). DPP III is a zinc-dependent aminopeptidase with indicated role in pathophysiological processes, such as: pain, ovarian carcinoma, oxidative stress, inflammation and cataractogenesis [1]. Previous research has shown that cyclobutane derivatives containing amidino-substituted benzimidazole moieties are important for the inhibitory activity of human DPP III [2]. Since benzimidazole derivatives have shown wide variations in their structures, this study was aimed to elucidate the structural features of benzimidazole derivatives required for antagonism of dipeptidyl peptidase III inhibitors using Quantitative Structure-Activity Relationship (QSAR) analysis. QSAR is a cheminformatic technique for establishing the quantitative relationship between biological activity and descriptors representing physicochemical properties of the compounds in a series using statistical methods. "Two-dimensional" (2D), "three-dimensional" (3D) molecular descriptors, quantum chemical descriptors, and physicochemical parameters, derived from optimised three-dimensional structure, have been calculated using the Dragon program and HyperChem 8.0. Multiple regression analysis was performed using STATISTICA 7.0. Selection of predictor variables for multiple regression was performed by best-subset method. QSAR is aimed to elucidate the structural features of benzimidazole derivatives required for antagonism of dipeptidyl peptidase III inhibitors. In order to understand the mechanism of the most potent inhibitor binding into the active site of human DPP III we performed docking by AutoDock4 program and molecular dynamics simulation with the AMBER10 package. The presented study can guide the rational synthesis of novel inhibitors with increased affinity and efficacy.

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Primjena ugljikovih nanocjevčica u analizi ropinirola

Application of carbon nanotubes in analysis of ropinirole

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Ropinirole (ROP) is a novel nonergoline dopamine agonist indicated for the treatment of early and advanced Parkinson's disease and also for the treatment of primary restless legs syndrome. Due to noticeable shortage of analytical methods for ROP determination, there is a constant demand for developing reliable methods to evaluate the quality of its pharmaceutical formulations and to quantify drug in biological samples.

Electroanalytical techniques are particularly suitable for quantification of many drugs. Since their discovery, carbon nanotubes (CNTs) have attracted enormous attention for the preparation of electrochemical sensors due to their unique structure and extraordinary electronic properties. A remarkable enhancement effect on the electrochemical response has been observed after dispersing CNTs in Nafion, a perfluorosulfonated polymer. A simple and sensitive sensor was developed and the electrochemical behaviour of ROP was investigated on the multi-walled carbon nanotubes/Nafion composite film modified glassy carbon electrode (MWCNTs-Nafion/GCE). Under optimized conditions, the response peak currents had linear relationship with drug concentration in the range of 1.0×10^{-7} – 1.0×10^{-5} M. A new electroanalytical method with good precision and accuracy was developed for direct quantification of ROP in tablets. The results were satisfactory in comparison with those obtained using high-performance liquid chromatographic method.

***In vivo* određivanje testne koncentracije ispitivanog spoja
zasnovan na „Up and down“ metodi**

***In vivo* determination of test concentration for tested compound
based on up- and- down- method**

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Pharmacology testing of a new compound implies the determination of toxicity and genotoxicity following potential antimicrobial, antitumor or some other healing effects. Pharmacology evaluation usually needs results of *in vivo* testing on different animal models. The most used animal model is the mouse model because of strong physiological resemblance with humans. Design of animal model must be conceived in the way that necessary answers about the desirable and undesirable characteristics of the test compound gain on the smallest possible number of animals [1]. Toxic evaluation requires the determination of non-lethal compound's concentration. One of the recommended methods for the toxicity studies is the up-and-down procedure [2]. In this work, a highly inbred strain of male mice (n=12) on mixed genetic background from strains C₅₇BL/6J and 129S₁/SvImJ was used. We tested two new monomethine cyanine derivatives (MCD 4, and 8) in a the concentration range 3.5; 7.0; 15.0, and 30.0 mg/kg of MCD 4, and 3.5 and 7.0 mg/kg of MCD 8 diluted in 0.9% NaCl. Mouse survival 24hrs after intra peritoneal application was monitored. Mice were further subdued to the time and concentration tolerance test during 40 days. On the thirteenth and twenty six day test animals received 2nd and 3rd dose of the tested compound. Tested animals were daily monitored for their behaviour and weighed. During the test period mice treated with MCD 4 at the concentrations of 15 and 30 mg/kg died, followed by average loss of body weight by 18.55% and 32.26%, respectively. Mice treated with smaller test concentrations of MCDs survived the 40 day test period. According to the obtained results the concentration of 7.0 mg/kg was selected as the appropriate compounds' concentration for further acute and chronic toxicology study.

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**Modulacija gena stresnog odgovora polifenolima tijekom
regeneracije jetre u miša**

**Modulation of stress-response genes by polyphenols during
liver regeneration in mice**

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Polyphenols interact with nutrient-sensitive transcription factors that coordinate antioxidant response and thus may be of value in conditions which are challenged by changes in the oxidative state. Therefore, we addressed the ability of the olive oil polyphenols extract (PFE) to induce NF- κ B-mediated antioxidant genes expression and concomitant changes in the oxidative state during liver regeneration after 1/3 hepatectomy in mice.

Prior to hepatectomy mice were intraperitoneally administered either PFE (50 mg/kg bw), or saline during seven consecutive days, while respective controls received vehicle alone. The levels of serum α -glutathione-S transferase (GST), hepatic malondialdehyde and total glutathione, along with the activities of glutathione reductase (GR) and mRNA levels of NF- κ B gene and its targets, γ -glutamylcystein synthetase (GCS) and superoxide dismutase 2 (SOD2) were determined at 0 (controls), 1, 3, 6, 12, 24 and 48 hours after the surgery. Withal, liver mass restoration was calculated.

Up to 3 hours after hepatectomy, PFE pre-treatment elevated malondialdehyde, but depleted GSH level and impaired the processes that affect glutathione homeostasis, as indicated by the decreased GR activity, suppressed GSC transcriptional activity, and increased glutathione utilization via the GST mediated reactions. These changes were accompanied by the NF- κ B and SOD2 gene upregulation in all time intervals, leading to the normalization of the parameters of oxidative stress and recovery of glutathione status in the periods following 6 hours post-hepatectomy, ultimately resulting in increased liver mass recovery.

Increased oxidant load upon polyphenols pre-treatment is associated with the induction of NF- κ B mediated adaptive stress response which contributes to antioxidant protection and supports the liver growth.

Procjena oštećenja bubrežnih stanica kod osoba s kalcij oksalatnom urolitijazom

Assessment of renal cell injury in patients with calcium oxalates urolithiasis

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Urolitijaza (stvaranje i rast bubrežnih i/ili mokraćnih kamenaca u organizmu čovjeka) je složen i multiuzročno javno-zdravstveni problem. Poznata je fizikalno-kemijska i metabolička osnova bolesti. Liječnici, kemičari i biolozi razmatrali su niz procesa i poremećaja (prezasićenje urina te uloga promovirajućih i inhibirajućih tvari) odgovornih za urolitijazu. Međusobni omjeri suviška promotora i manjka inhibitora često se prikazuju kao indeksi rizika za razvoj urolitijaze, što ukazuje i na inhibitorni potencijal urina. Ipak, sam proces nastanka kamenaca nije još u potpunosti razjašnjen.

U procesu stvaranja mokraćnih kamenaca važna je i retencija stvorenih kristala u urinarnom traktu. Oštećenja bubrežnih stanica izazvana oksidativnim stresom uslijed prisutnosti promotora kristalizacije u povišenim koncentracijama, u urinarnom traktu i upalnim procesima dovode do veće predispozicije za interakcije kristal-stanica, što pokazuju osjetljivi biomarkeri bubrežnog oštećenja kao što su L-FABP, nGAL, cistatin C.

U radu je istraživana stupanj oštećenja epitelnih stanica bubrežnih tubula nastalih uslijed toksičnog djelovanja hiperoksalurije kod osoba s kalcijском urolitijazom pomoću spomenutih biomarkera bubrežnog oštećenja kao nov način procjene sklonosti stvaranju mokraćnih i/ili bubrežnih kamenaca. Rezultati metaboličkih parametara urolitijaze u prvom jutarnjem urinu bili su izraženi na gram kreatinina. Ispitanici (125 osoba) su pokazali više vrijednosti promovirajućih čimbenika kalcijske litijaze, indeksa rizika kao i povišene vrijednosti biomarkera od dobivenih vrijednosti za iste parametre kod kontrola (62 osobe).

Kao zaključak može se reći da je moguće da se na osnovu procjene stupnja oštećenja bubrežnih tubularnih stanica s gore navedenim biomarkerima predvidi moguću retenciju stvorenih kristala u urinarnom traktu osoba s kalcijском urolitijazom.

Fizikalno-kemijska analiza inkrustata na urološkoj dvostrukoj J protezi

Physico-chemical analysis of encrustates on urological double J stent

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Kod ljudi jedan od patoloških oblika biomineralizacije u organizmu predstavlja proces u kojem se iz kompleksnog kemijskog sustava, kakav je urin, talože anorganske soli kao mokraćni i/ili bubrežni kamenci različitih sastava, što je uvjetovano fizikalno-kemijskim, genetskim, endokrinim, anatomskim, klimatskim, upalnim i dr. čimbenicima. Bolest se definira kao urolitijaza i predstavlja još i danas ozbiljan zdravstveni, društveni i sociološki problem.

Mnoge komplikacije urolitijaze suvremena urologija rješava intubacijom mokraćovoda artefijalnom protezom. Dvostruka J proteza mokraćovoda je tanki gumeni, plastični ili silikonski kateter koji omogućuje protok urina pokraj istaloženih prepreka kroz mokraćni sustav. Iako su JJ proteze izrađene od inertnih sintetskih biomaterijala, kod osoba koje su sklone stvaranju kamenaca, na njima se također talože anorganske naslage (inkrustati) zbog čega je njihova uporaba u organizmu vremenski ograničena.

U istraživanjima u ovom radu načinjene su kemijske analize sastava naslaga na JJ protezama uklonjenih iz mokraćnog sustava kod izabrane skupine ispitanika. Analize su načinjene s dvije instrumentalne analitičke metode: termogravimetrijskom analizom i FT-IR spektroskopijskom analizom. Uzorci naslaga uzimani su s tri različita mjesta na protezi: s početka, iz sredine i s kraja. Kod ispitanika s inkrustatima češća je bila pozitivna urinokultura, stentovi su bili duže postavljeni kod ispitanika (grupa s inkrustatima) nego kod grupe bez inkrustata (kontrola). Rezultati analize sastava naslaga na protezama uspoređeni su s rezultatima analize sastava kamenca te je pokazano da oni nisu jednoznačni.

Kao zaključak može se reći da neki parametri se nisu značajno razlikovali u osoba s inkrustatima i bez inkrustata, najčešći sastojak inkrustata je apatit, zatim struvit, brušit a najrjeđi su inkrustati kalcij oksalata. Sastav inkrustata nije uvijek istovjetan ni po nivoima.

Sekcija: Kemija u poljoprivredi i šumarstvu
Topic: Chemistry in agriculture and forestry

Digitalna SMS vaga kao suvremeni alat na pčelinjaku

Digital SMS scale as a modern tool at an apiary

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Klimatske promjene i suvremen način pčelarenja pred pčelare stavljaju često nepremostive izazove. Moderno pčelarstvo u svojoj osnovi podrazumijeva selidbu košnica radi boljeg iskorištavanja medonosne paše i čest obilazak košnica. Danas u vrijeme skupih energenata ovi zahtjevi znatno poskupljuju cijeli proizvodni proces. Digitalna SMS vaga smanjuje troškove obilaska pčelinjaka na minimum i istovremeno daje pčelaru čitav niz podataka koji mu pomažu u donošenju odluka važnih za tehnološki proces proizvodnje meda i drugih pčelinjih proizvoda na pčelinjaku. Pčelaru vaga daje podatke o promjeni u masi košnice, kao i osnovne meteorološke podatke izmjerene u košnici i u njenom okolišu. Promjene u masi košnice pčelaru daju informacije u tome je li počelo izlučivanje nektara očekivane medonosne biljke ili nije tj. kada je završila paša i kada je trenutak da se košnice presele na drugu pašu. Nadalje, pčelar dobiva informaciju o snazi pčelinjih zajednica koje seli i na osnovu toga može prognozirati uspjeh koji će uslijediti kod vrcanja meda i prema potrebi mijenjati tehnologiju uzgoja jakih pčelinjih zajednica. Na osnovi dobivenih meteoroloških podataka pčelar može donijeti odluku o odlasku na pčelinjak ukoliko su oni povoljni. Pčelaru su od velike pomoći tijekom zimovanja pčelinje zajednice senzori za temperaturu i vlagu zraka instalirani unutar pčelinjeg klupka i u košnici tijekom zime. Ovi senzori za temperaturu i vlagu zraka u proljeće pčelaru omogućuju uvid u događaje u košnici i bez potrebe za njenim otvaranjem koje uzrokuje uznemiravanje i rashlađivanje pčelinje zajednice.

Zbog ovako velikog značaja digitalne sms vage u suvremenom pčelarstvu, kao dio IPA projekta „Panonian Bee“ prekogranične suradnje Hrvatska-Srbija, kreirana je mreža od 20 digitalnih sms vaga koje svoje podatke šalju na posebno dizajniranu web stranicu. Podaci su javni i svima dostupni, a rad će prikazati do sada dobivene rezultate.

Uloga sumporovodika u toleranciji biljaka na solni stres

The role of hydrogen sulfide in salt stress tolerance in plants

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Hydrogen sulphide (H₂S) is known to be produced by both animal and plant tissues suggesting that this compound may be involved in cell signal transduction. There is a growing body of evidence to suggest that the presence of this gasotransmitter may modulate oxidative stress metabolism in cells. In collaboration between English and Croatian Universities, it was found that pepper plants pre-treated with H₂S donors, such as NaSH and GYY4137, and exposed to the salt stress, showed significant differences in lipid peroxidation levels, hydrogen peroxide and proline concentrations. Cucumber seeds pre-treated with H₂S donors and germinated in NaCl solution, showed a significant influence of H₂S treatments on the same parameters as in pepper. The results suggested that H₂S may have a regulatory role in stressed plants and may affect the accumulation of protective metabolites such as proline. Crucial tools in this kind of research are H₂S-releasing compounds with different chemical properties, such as cell permeability or H₂S releasing rate, along with *in vivo* methods of detection of H₂S using highly specific fluorescence probes. As well as for purely academic reasons these compounds may have practical applications in agriculture through the fostering of plant environmental stress tolerance.

**Primjena polietilen glikola-6000 u istraživanju osmotskog stresa
kod soje (*Glycine max* (L.) Merr.)**

**Polyethylene glycol-6000 application in the research of osmotic stress
in soybean (*Glycine max* (L.) Merr.)**

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Polyethylene glycols (PEG) are produced by polymerization of ethylene oxide (EO) with water, mono ethylene glycol or diethylene glycol under alkaline catalysis. The result is a very simple chemical structure: HO-[CH₂-CH₂-O]_n-H, where (n) is the number of EO-units. The most important property of all PEGs is their solubility in water, which makes them ideally suitable for use in countless different applications. PEGs have been widely used in the study of the water relations of plants, especially for simulating drought (osmotic stress) conditions. The osmotic potential of aqueous solutions of PEG 6000 is related to its concentration. Here, we presented the results of physiological response of soybean seedlings to PEG-imposed osmotic stress. Beside water (control), two levels of osmotic stress were applied - 5% (-0.5 bars) and 10% (-1.48 bars) PEG 6000 solution as a medium for seed germination. The level of free proline, total phenols and lipid peroxidation in hypocotyl tissue increased with PEG concentration (osmotic stress intensity). As the tested soybean cultivars differed in particular metabolic parameter responses, PEG might be considered as a convenient tool for the screening of soybean cultivars diversity in osmotic stress tolerance, which is important for successful field production of this valuable crop species.

Proizvodnja sigurne hrane na temelju kemijske analize tla

Safe food production based on chemical analysis of soil

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World food demand is increasing rapidly, and when we take into account climate changes and the constant rise in prices of inputs, with increasing environmental awareness of the population and food security, crop production becomes very challenging. The aim of this paper is to show the importance of soil chemical analysis in calculating the need for nutrients (especially nitrogen) required for optimum plant production. During the period of 10 years ~ 25,000 soil samples were collected and formed into a database, which along with all necessary information about the land, contains information on land owner, latitude and longitude of sampling and soil chemical properties: (pH H₂O and KCl, organic matter content, P₂O₅, K₂O, hydrolytic acidity and carbonate content). Using the ALRxp professional software for fertilizer recommendation calculation and soil suitability assessment, an output data-base was formed which has been used for geostatistical analysis, visualization and estimation of the required quantities of the most important nutrients (N, P, K) for plant production in Osijek-Baranja County. Without the soil analysis this assessment method would not be possible, since the soil chemical data are the most important part of the database. Obtained data can also be used for regionalization, land monitoring, and for the assessment and planning of crop production in a certain area.

Sekcija: Zaštita okoliša
Topic: Environmental protection

Zooplankton kao indikator ubrzanih procesa eutrofikacije

Zooplankton as indicator of accelerated eutrophication distortions

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Anthropogenic impact causes accelerated and overall environmental changes. Eutrophication, as one of the consequences of anthropogenic impact due to increased input of organic matter, reflects in the increasing concentrations of nutrients (nitrate, phosphate) and hydrosystem production. It is particularly pronounced in shallow lakes and leads to water quality distortions. Shallow water bodies are important landscape features which determine microclimate conditions and affect biocenoses associated with them. Biotic indexes based on the diversity and abundance of zooplankton organisms (rotifers – Rotifera, cladocerans – Cladocera, copepods – Copepoda) as well as their food preferences provide important information in water quality assessment. To determine the accelerated eutrophication processes, physico-chemical parameters and zooplankton were studied within the two years distance. Samples were collected in a shallow lake (Krapina River watershed), which has a function of sport fishing and is surrounded by agricultural land. The objectives of the study were: (i) to determine the effect of environmental factors on the structure of zooplankton and (ii) to compare the abundance and diversity of zooplankton in a time period. The assessed changes in environmental conditions (transparency reduction, increasing the concentration of nutrients and organic matters) indicate an increase in eutrophication within a short time period. Increasing rotifer and cladoceran microfilter-feeders also pointed out higher concentrations of organic matter that serves them in their diet. Results of this study stress the importance of zooplankton organisms as very sensitive and reliable indicators of environmental alterations in water quality assessment. Changes in environmental conditions affect the alteration in zooplankton as well as in aquatic biocenosis structure and could imply terrestrialisation of shallow water bodies in a relatively close future.

**Vremenske varijacije koncentracija ozona, dušikovog dioksida
i ugljikovog monoksida u urbanom području**

**Temporal variations in concentrations of ozone, nitrogen dioxide
and carbon monoxide in an urban area**

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Air pollution has been a common theme for the past decades, because it is a growing source of general pollution and its most common origin in urban areas are gases from vehicle exhausts. The main pollutants from diesel fuelled vehicles include carbon monoxide (CO) and nitrogen dioxide (NO₂), from which a secondary pollutant, ozone (O₃), is formed.

This study investigates different behavioural analysis patterns of the leading species in photochemically polluted air (CO, NO₂, and O₃) in order to find their dependence on anthropogenic activity and/or meteorological conditions.

During summer months, the excessive concentration of oxidants is formed in the atmosphere of many urban and rural areas, so the corresponding measurement data of CO, NO₂ and O₃ are compared from June to September of 2002, 2007, and 2012 in the city of Osijek. Another approach for the assessment of ambient air quality is by calculating photochemical pollution indicators during the summer seasons of the same years. These indicators include, as a basic parameter, the average of the daily maximum to minimum ratio calculated from hourly ozone concentration measured over a period of time. Furthermore, an attempt was made to establish a correlation between measured pollutant concentrations and meteorological parameters using the technique of multivariate principal component analysis (PCA). The results of PCA revealed underlying relationships between O₃ concentrations and meteorological data and showed that ozone concentrations are associated with temperature, solar radiation, and visibility. Pollutants CO and NO₂ significantly correlate with each other.

Ispitivanje različitih bioadsorbensa za uklanjanje bojila malahitnog zelenila i metilenskog plavila iz vodenih otopina

A survey of different bioadsorbents for removal of malachite green and methylene blue dyes from aqueous solutions

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Synthetic dyes have wide application in many industries, such as pharmaceutical, cosmetic, textile, paper, leather, plastics etc. The presence of dyes in the effluents (namely wastewater) of the above mentioned industries is a major concern due to their high thermal stability and photostability, i.e. their persistence in the environment for an extended period of time. Furthermore, they are recalcitrant towards removal during usually employed wastewater treatment methods. Many agricultural waste materials containing high proportions of cellulose have the ability to adsorb various dyes and represent a simple and low-cost method of coloured wastewater treatment. The aim of this study was to preliminarily investigate different low-cost bioadsorbents for their potential to remove the synthetic dyes of malachite green (MG) and methylene blue (MB) from aqueous solutions. Six lignocellulosic waste materials, beech sawdust (*Fagus sylvatica* L.), oak sawdust (*Quercus robur* L.), poplar sawdust (*Populus alba* L.), sugar beet waste, apple pomace and spent beer grains were tested for their ability to remove MG and MB from 15 mg L⁻¹ aqueous dye solutions at constant temperature of 25 °C. Activated carbon served as control. Adsorbents were soaked in dye solutions for 5 hours and samples were taken at 30 min intervals for spectrophotometric determination of colour removal. All tested adsorbents showed high colour removal capacity at 5 hours contact time for both used dyes (90.74 – 98.06 % and 94.26 – 100 % for MG and MB, respectively). The results indicate that the used bioadsorbents may have the potential to be used as adsorbents for the efficient remediation of coloured wastewater.

**BIOCOS[®] uređaj za pročišćavanje otpadnih voda Našice:
od puštanja u pogon do stabilnog rada**

**BIOCOS[®] wastewater treatment plant Našice:
from start-up to stable operation**

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The ongoing population growth and economic development represent a challenge regarding the environmental protection. With the increase of water consumption, the wastewater amount is subsequently increasing. Before being discharged into natural recipients, the wastewater undergoes treatment at wastewater treatment plants. The wastewater treatment plant of the city of Našice uses BIOCOS[®] (*Biological Combined System*) technology, which represents an improvement of the conventional activated sludge technology and is the only example of this technology for 15 000 PE agglomeration in the Republic of Croatia. The main difference between the conventional activated sludge system and BIOCOS[®] is the activated sludge – water separation process and the sludge recycle. The need for a secondary clarifier and return-sludge pumping station is avoided in BIOCOS[®] system, while their function is assumed by the circulation and settling tank connected to the aeration tank and blowers. This paper gives a detailed overview of the BIOCOS[®] technology and wastewater treatment plant performance from its start-up to stable operation by monitoring the basic process parameters.

Utjecaj poplavnih voda na kvalitetu podzemnih voda

Influence of flooding waters on natural water reserves

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Globalne promjene klimatskih prilika uzrokuju nenadane, i za ove generacije nedoživljene elementarne nepogode. Klimatske promjene nedvojbeno su pridonijele povećanju vjerojatnosti i negativnih učinaka ove pojave u području sjeverne Hrvatske. Poplave negativno utječu na zdravlje ljudi, okoliš, kulturnu baštinu i gospodarsku aktivnost. Poplavljena područja su ujedno i područja intenzivne poljoprivrede. Mnoga domaćinstva na tom području imaju vlastiti izvor vode (bunar ili bušotinu) koji mogu koristiti za svoje potrebe u neograničenim količinama. Međutim, poplavne vode ispiru poljoprivredno zemljište odvođeci u podzemlje, a time i u bunare, velike količine umjetnih gnojiva, herbicida, pesticida. Načinjena je spektrofotometrijska analiza nitrata [1-3] poplavnih voda s područja Čička Poljana i Petrovina turopljska pri čemu je, očekivano, utvrđena povećana koncentracija nitratnih iona 97 mg/L. Također je istom metodom načinjena analiza bunarske vode nakon povlačenja poplavnih voda. I u bunarskoj vodi utvrđena je povećana koncentracija nitratnih iona 67 mg/L. Takva voda ne smije se upotrebljavati u kućanstvu, a pogotovo piti. Nitrati se moraju ukloniti iz bunarskih voda.

Nitrati se iz otpadnih voda mogu ukloniti postupkom ionske izmijene [4]. Tim postupkom uspješno se uklanjaju nitrati na razinu ispod maksimalno dozvoljene koncentracije. U ionskoj izmjeni kao sredstvo za regeneraciju koristili smo otopinu KCl koji u reakciji sa nitratnim ionima daje $\text{KNO}_3(\text{aq})$, tj. otopinu umjetnog gnojiva koja se može iskoristiti.

- [1] V.I. Mijatović, Z. Šljivović, Propis za vježbe iz tehnologije vode i goriva, Inertna skripta PBF, Zagreb.
- [2] Z. Weihnacht, S. Rupčić Petelinc, S. Žužek, Praktikum iz analitičke kemije, Školska knjiga, Zagreb, 2009.
- [3] Skoog-West-Holler, Osnove analitičke kemije, Školska knjiga, Zagreb, 1999.
- [4] M. Matošić, Dentrifikacija vode za piće selektivnom ionskom izmjenom, magistarski rad, Prehrambeno tehnološki Fakultet, Sveučilište u Zagrebu, 1999.

Određivanje i statistička analiza PM_{2.5} i PM₁₀ kao pokazatelja onečišćenja zraka na širem splitskom području

Determination and statistical analysis of PM_{2.5} and PM₁₀ as an indicator of air pollution in Split region, Croatia

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The study presents a statistical analysis of air quality parameters, including PM_{2.5} and PM₁₀ concentrations (measured at three stations in Split region), along with NO, NO_x, NO₂, SO₂ and black smoke (BS) data, for a 5-year period. Average concentrations of PM_{2.5} at three different stations were found to be 28.2, 19.9 and 14.3 µg m⁻³, while those found for PM₁₀ were 15.2, 25.8 and 14.5 µg m⁻³. High correlations between PM_{2.5} and PM₁₀ (0.62 and 0.54, respectively) were determined between the industrial (A2) and residential (A3) stations, while lower correlation (between PM_{2.5} and PM₁₀ was 0.22) was noticed at the station placed in traffic and industrial (A1). At the A1 station for the year 2009, A2 for 2010 and A3 for 2006 the values of PM_{2.5} exceed the allowable limits by the Croatian legislation and EU Directive (25 µg m⁻³). Annual mean concentration levels of PM₁₀ were below allowable limit (40 µg m⁻³) at all stations except for A3 in the year 2006.

Contributions of different sources were determined using multivariate receptor modelling (Principal Component Analysis, Cluster Analysis) and it was found that major sources of pollution were in accordance with the stations' positions. Comparison of particle mass concentrations with those reported for different European cities indicate lower loading with PM in the Split region.

Ocjena kvalitete pitke vode iz privatnog zdenca

A quality assessment of a drinking water from a private well

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The quality of drinking water from a private well in northern Slovenia was studied. It was suspected that water could be polluted by some specific pollutants as a consequence of fertilization. Physico-chemical analyses were performed in the laboratory for water treatment in order to determine the water quality. The results of the physico-chemical analysis showed no elevated values. The ammonium (N-NH₄), nitrate and nitrite concentrations, potassium concentration as well as chemical oxygen demand (COD) values were below the maximum allowed concentration values (MAC) for drinking water [1]. The presence of the *E. coli*, *Coliform bacteria*, *Enterococci*, and *Pseudomonas aeruginosa* was checked in the microbiological laboratory. The first sample was taken during a rainy period. The *Coliform bacteria* and *Enterococci* were developed over 24 hours at room temperature. In the water samples taken during the dry period in March, none of above mentioned microorganisms were determined. During a rainy day the samples were taken again. The results showed the presence of *Coliform bacteria* and *Enterococci*. Their concentrations exceeded the values of the drinking water regulations in water samples. After inspecting the water reservoir it was found that the lid had a crack. The drinking water could have been polluted with *Coliform bacteria* and *Enterococci* due to rain trickling through the lid. Restoration and cleaning of the whole reservoir were done, and for this reason, the water quality had to be checked again. The results showed that the water was wholesome.

- [1] Official gazette of Republic of Slovenia, Rules of drinking water quality (2004), Uradni list RS, No 19/2004, with supplements - (35/04), (26/06), (92/06), (25/09), p.2155.

Kompostiranje u školi

Composting at school

Biljana Pavić

Međunarodna Eko-škola OŠ August Šenoa, Drinska 14, 31000 Osijek, Hrvatska

Kompost je vrlo vrijedno prirodno gnojivo koje je nastalo biološkom razgradnjom otpadnih organskih tvari iz kućanstava tijekom pripreme hrane, organskih tvari iz vrtova ili parkova. Prema nekim analizama organski otpad čini trećinu komunalnog otpada. Kompostiranje je pravi način sustavnog gospodarenja organskim otpadom, ali i izvrsna prilika da se tlu vrate vrijedne organske tvari koje su pretvorene u prirodno gnojivo. U skladu sa sedmim milenijskim razvojnim ciljevima koji su posvećeni održivom razvoju u Međunarodnoj Eko-školi OŠ August Šenoa iz Osijeka već četrnaest godina učenici i djelatnici škole proizvode kompost koji koriste za prihranu školskog cvijeća i drveća u edukativnom parku, kao i uzgoj cvijeća, bundeva i tikvica. Svoja iskustva o kompostiranju rado dijele s drugima, te su im česti gosti vrtičarci, učenici osnovnoškolskog i srednjoškolskog uzrasta i studenti. Također odlaze u druge škole, na Jesenski sajam u Osijeku i na županijska stručna vijeća učitelja te putem radionica poučavaju druge u kompostiranju. Kompostiranjem ujedno razvijaju i poduzetničke kompetencije u skladu sa razvojnim kurikulumom škole. Aktivno surađuju i sa Centrom za kompost iz Osijeka, a u suradnji s njima i UNIKOM-om d.o.o. snimili su i spot o kompostiranju.

**Usporedba instrumentalnih tehnika ICP – OES i AAS
u određivanju metala u uzorcima čestične tvari u zraku**

**The comparison of instrumental techniques ICP – OES and AAS
in the determination of metals in air dust**

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Kvaliteta zraka ima značajnu ulogu po ljudsko zdravlje i okoliš u cjelini. Praćenjem kvalitete zraka i njene zaštite provode se mjere za sprječavanjem štetnog utjecaja. U tu svrhu praćenje koncentracija teških metala u čestičnoj tvari atmosfere i njihov utjecaj na kakvoću zraka ima važnu ulogu. U analizi uzoraka iz okoliša važnu ulogu ima njihova priprema. Određivanje metala - Cd, Co, Ni, Fe, Sb i Sn, provedeno je u uzorku dobivenom u sklopu međulaboratorijskog ispitivanja (*proficiency testing* - PT), IFA – *Metal dust*. Isti uzorak je pripremljen na dva načina. Prvi je mikrovalna digestija pri uvjetima koje propisuje norma EN 14902 s otapalima HNO₃ i H₂O₂ pri temperaturi od 220 °C i maksimalnom tlaku od 55 bara. Drugi način pripreme je metoda refluksa s HNO₃ i HCl. Za kvantitativno određivanje korištene su dvije tehnike ICP-OES i AAS-GF. Svi metali određeni su ICP-OES tehnikom, dok su Cd, Fe i Ni određeni i tehnikom AAS-GF-a. Primjena obaju načina pripreme uzorka pokazala se uspješnom iako se metoda refluksa pokazala uspješnijom. Uspoređujući analitičke tehnike u određivanju koncentracija teških metala korištenje obiju tehnika pokazalo se također uspješnim, premda su iskorištenja dobivena tehnikom ICP-OES kod određivanja Cd, Ni i Fe bolja od onih dobivenih tehnikom AAS-GF.

Heterogena fotokataliza pomoću TiO₂ za fotokatalitički tretman otpadnih voda

Heterogeneous photocatalysis using TiO₂ for photocatalytic wastewater treatment

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In recent years scientific research has focused its attention to the use of semiconductor materials as photocatalysts for the removal of organic and inorganic species from aqueous systems in wastewater treatment.

The most widely used semiconductor is TiO₂. The main advantages of this metal oxide as a semiconductor are: (i) its mechanical and chemical robustness; (ii) lack of toxicity; (iii) its wide availability; (iv) high photochemical stability and lack of photocorrosion [1].

In order to activate the degradation process, pure TiO₂ requires photo-excitation with light at wavelengths < 387 nm. However, UV in natural sunlight represents only 5% – 8% of the solar spectrum at sea level and this provides a limitation and the requirement of artificial illumination of the catalysts in order to achieve degradation of the organic material in times that are practical for water treatment processing. The need for more stable, efficient catalysts which can be activated by natural sunlight is now the goal of researchers [2].

Visible light-activated TiO₂ could be prepared by doping or sensitizing. As far as doping of TiO₂ is concerned, in obtaining tailored material with improved properties, metal and nonmetal doping has been performed in the context of improved photoactivity.

All of organic compounds and water can undergo oxidation under aerated photocatalytic conditions leading to the generation of hydroxyl radicals and reactive oxygen species.

As a method for contaminant control in water, heterogeneous photocatalysis using titanium dioxide is more efficient than conventional methods. This is because as the photocatalytic process gradually breaks down the contaminant molecules, no residue of the original material remains and therefore no sludge requiring disposal to landfill is produced. The catalyst itself is unchanged during the process and no consumable chemicals are required.

[1] A. Primo, H. García, New and feature developments in catalysis, Elsevier, Amsterdam, The Netherlands, Oxford, UK, Waltham, USA, 2013, str 146.

[2] Alex Omo Ibhaddon, Paul Fitzpatrick, *Catalysts* 3 (2013), 189.

Utjecaj protoka na uklanjanje olova i cinka iz binarne vodene otopine na prirodnom zeolitu postupkom u koloni

Influence of flow rate on lead and zinc removal from a binary solution on fixed natural zeolite bed

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The removal of heavy metals from wastewaters to concentrations below the permissible limits requires the application of advanced technological treatment processes such as ion exchange and adsorption. Due to their high costs, recent investigations have been directed to finding solutions for making them suitable for wide application. Excellent physical and chemical properties of natural zeolites, high ion exchange capacity, wide distribution of deposits in nature, simple and easy exploitation makes them sustainable ion exchangers and adsorbents. The column performance of ion exchange allows successive repetitions of several service and regeneration cycles and thus treatment of a large quantity of wastewater, which makes natural zeolites even more attractive. The removal of heavy metal ions from multicomponent systems is very complex due to different ion exchange affinity and different selectivity of zeolite. The aim of this study was to examine the influence of flow rate on Pb and Zn removal from a binary solution on natural zeolite.

Laboratory column tests were performed at room temperature in a 50 cm long glass column with an internal diameter of 1.2 cm, filled with a zeolite sample up to 8 cm. The equimolar feed solution $c_0(\text{Pb}^{2+} + \text{Zn}^{2+}) \approx 1 \text{ mmol/L}$, flowed from the top to the bottom of the column at the constant flow rates of $Q = 1, 2 \text{ and } 3 \text{ mL/min}$, using a vacuum pump. After each service cycle, the regeneration of exhausted zeolite was performed with NaNO_3 , $c = 176.5 \text{ mmol/L}$, at the flow rate of 1 mL/min . In all experiments the effluent was periodically collected at the bottom of the column and analyzed for Pb and Zn concentrations.

With increased flow rate, breakthrough and exhaustion points appear earlier as expected. Capacities in breakthrough and exhaustion, q_B and q_E , are reduced as well as the removal efficiency, due to shorter contact time between the feeding solution and the zeolite layer. The results showed greater selectivity of clinoptilolite toward lead ions, and thus the displacement of Zn bound on zeolite with Pb from the feeding solution, but displacement effect is reduced with the increase in the flow rate. This is confirmed by regeneration curves.

Biorazgradnja eritromicina pomoću *Pseudomonas aeruginosa* FN

Biodegradation of erythromycin by *Pseudomonas aeruginosa* FN

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Prema strukturi i mehanizmu djelovanja, farmaceutici predstavljaju skupinu složenih molekula sa specifičnim djelovanjem u biološkim sustavima. Ukoliko farmaceutici dospiju u okoliš, predstavljaju potencijalnu opasnost zbog moguće akumulacije u okolišu i štetnog djelovanja na organizme u ekosustavu. Biorazgradnjom se onečišćujuće tvari mogu prevesti u manje složene i netoksične produkte pomoću mikroorganizama. Određeni mikroorganizmi posjeduju specifične enzime koji im omogućuju razgradnju složenih organskih molekula na jednostavnije, kao što su ugljikov dioksid i voda.

U ovom radu proveden je pokus biorazgradnje pomoću bakterije *Pseudomonas aeruginosa* FN. Tijekom pokusa praćeni su optička gustoća, koncentracije biomase i eritromicina te su provedeni testovi osjetljivosti i mikroskopska analiza. U pokusima biorazgradnje početne koncentracije eritromicina kretale su se od 2 µg/L do 200 mg/L. Početna koncentracija biomase je iznosila $6,49 \pm 0,49$ mg/L. Dobivena vrijednost IC_{50} iznosila je 124,2 mg/L. Testovi osjetljivosti pokazali su da je *P. aeruginosa* FN otporan na eritromicin. Učinkovitost biorazgradnje u provedenim pokusima u prosjeku je iznosila 33,31%.

Razgradnja prirodnih organskih tvari u vodi korištenjem heterogenog fentonovog katalizatora na zeolitnom nosaču

Natural organic matter degradation using heterogeneous Fenton catalysts on zeolite support

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Natural water throughout the world contains natural organic matter (NOM) in various concentrations. NOM changes the aesthetic characteristics of water, such as taste, smell and color. During water chlorination process harmful disinfection by-products (DBP) could be formed in a reaction between organic matter and chlorine.

Fenton process has shown good efficiency in degradation and removal of natural organic matter from water. However, homogeneous Fenton systems have some drawbacks which can be overcome by the usage of heterogeneous catalysts, where iron catalyst is immobilized on a support material.

An application of heterogeneous Fenton-type catalyst was investigated for the degradation of natural organic matter from two sources: model humic acid solution and natural groundwater from Osijek area. Supported iron catalysts were prepared by impregnation of different iron forms (Fe(III), Fe(II), FeOOH) on natural zeolite clinoptilolite as support material. The catalyst performance was compared and the effects of the most relevant operating conditions (catalyst concentration, H₂O₂ concentration, pH) were estimated. The usage of heterogeneous catalysts allows the process to be operated at pH conditions close to neutral and in those conditions heterogeneous Fenton processes yielded similar and even better results.

Ekonomski razvoj i zaštita okoliša

Economic development and environmental protection

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Zaštita okoliša svakim danom sve više postaje ključno pitanje kojim se suočavaju što lokalne i regionalne, pa tako nacionalne i globalne razine. Brzi rast stanovništva i ekonomsko-gospodarski razvoj u proteklih pola stoljeća doveli su do velikih prijetnji klimatskoj stabilnosti i ekosustavu kako u razvijenim, tako i u zemljama u razvoju. Održiv razvoj se definira kao razvoj temeljen na pažljivom planiranju ekonomskog razvoja EU, a u skladu sa zaštitom okoliša. Međutim, iskustva iz svijeta kao i Europe pokazala su da ljudi češće biraju brži ekonomski razvoj usprkos očuvanju okoliša, što je posebno vidljivo na slabije razvijenim područjima. Cilj rada je pokušati objasniti kako, ali i na koji način su pojedine države, regije ali i lokalno stanovništvo uspjeli spojiti ekonomski razvoj s očuvanjem okoliša. Učinak gospodarskog razvoja na okoliš široko je objašnjen pojam u ekonomskoj literaturi. Cilj je na dosadašnjim primjerima ukazati na potencijal za sukobe između zaštite okoliša i gospodarskog rasta, kao i međuzavisnost pojedinih ekoloških problema. Također, jedan od ciljeva rada je, na postojećim primjerima iz zemlje i inozemstva, pokušati dokazati da se ekonomski razvoj i zaštita okoliša nalaze na „suprotnim stranama“, te da je bez obzira na takve i slične situacije moguće razvijati ekonomske sustave u koliziji sa zaštitom okoliša.

4. Susret mladih kemičara
4th Meeting of young chemists

Utjecaj koncentracije katalizatora kalijevoga jodida na brzinu raspada vodikovoga peroksida

Influence of the catalyser potassium iodide concentration on the decomposition of hydrogen peroxide

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Vodikov peroksid je nelinearna molekula građena od vodika i kisika i pri standardnim uvjetima je bezbojna tekućina. Oksidacijski broj kisika u molekuli vodikovoga peroksida je $-I$, te ima i oksidacijsko i reduksijsko djelovanje. Posljedica toga je njegova široka primjena u znanosti, zdravstvu i industriji, gdje je ekološki prihvatljiva alternativa. Važna je njegova primjena u tekstilnoj industriji pri izbjeljivanju tekstila i drugih materijala, u zamjenu za sumporov (IV) oksid, a također i kao moguće raketno gorivo. U takvim je procesima bitno kontrolirati brzinu raspada vodikovoga peroksida.

Vodikov peroksid se pri standardnim uvjetima vrlo sporo spontano raspada na vodu i kisik uz oslobađanje topline. Reakciju mogu ubrzati strani spojevi poput nečistoća i katalizatora. Cilj je našega rada ispitati ovisnost brzine raspada vodikovoga peroksida o koncentraciji katalizatora kalijevoga jodida, pri konstantnoj temperaturi. Koncentracije kalijevoga jodida, uz koje smo pratili brzinu raspada vodikovoga peroksida bile su u području od 0,01 do 0,1 mol/L. Tijek kemijske reakcije i koncentraciju vodikovoga peroksida ispitivali smo manganometrijskom metodom. Temeljem rezultata mjerenja, može se zaključiti kako se brzina raspada vodikovoga peroksida, iste početne koncentracije, linearno povećava s povećanjem koncentracije katalizatora kalijevoga jodida u ispitivanom području koncentracija.

4. Susret mladih kemičara / 4th Meeting of young chemists

Vrste mineralnih gnojiva i njihov utjecaj na okoliš

Types of fertilisers and their effects on the environment

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Istočna Hrvatska je područje intenzivne poljoprivrede te je upotreba prirodnih i umjetnih gnojiva u ovom području uzrok pojačane eutrofikacije voda. Kako bi utvrdili kakvo je pravo stanje u površinskim vodama uz poljoprivredne površine, učenici trećih razreda Gimnazije Vukovar napravili su istraživanje tako što su prikupili 9 uzorka površinskih voda uz poljoprivredne površine na području Vukovara i okolice. Uzorci su uzeti iz nekoliko melioracijskih kanala uz oranice kao i iz bara i ribnjaka, Bobotskog kanala i rijeke Vuke. Učenici su uzimali uzorke u travnju nakon kišnih dana. Pretpostavili su kako će ispiranjem tla uslijed kiša doći do povećanja vrijednosti nitrata i fosfata u vodama. U školi su ispitali uzorke na 4 parametra: nitrate, nitrite, amonijeve ione i fosfate. Podatci koji su dobiveni uspoređeni su s vrijednostima danim u *Pravilniku o parametrima ekološkog i kemijskog statusa površinskih voda*. Analizirajući prikupljene uzorke zaključili smo da je u većini uzoraka kvaliteta vode *dobra do umjereno dobra* što nam govori da se racionalno i odgovorno upotrebljavaju umjetna gnojiva na području Vukovara i okolice. Jedan uzorak pokazuje ekstremno visoke koncentracije ispitivanih vrijednosti. Kanal iz kojega je uzet uzorak povezan je s rijekom Dunav te predstavlja izravan izvor onečišćenja. Od mještana smo dobili informacije da se u taj kanal izlijevaju otpadne vode iz kućanstava što objašnjava visoke vrijednosti nitrata i fosfata dobivenih analizom.

Fosfati u rijeci Dunav kod Vukovara

The content of phosphates in the river Danube near Vukovar

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Tehnička škola Nikole Tesle Vukovar, Blage Zadre 4, 32000 Vukovar, Hrvatska

Voda je jedna od najjednostavnijih i najrasprostranjenijih tvari u prirodi čije su fizikalne i kemijske značajke dobro poznate. Neke od tih značajki su jedinstvene pa je upravo zbog tih posebnih obilježja voda tako važna za održavanje života na Zemlji. Zbog neprestanog kruženja vode u prirodi količina vode se ne smanjuje, ali se njena kvaliteta neprestano pogoršava. Jedan od pokazatelja kvalitete prirodnih voda jest sadržaj fosfata. Prevelike količine fosfata mogu izazvati ekološke katastrofe. Fosfati se u vodi najčešće određuju spektrofotometrijskom metodom, tvorbom fosfomolibdenskog modrila.

Dunav je jedna od većih europskih rijeka koja protječe i kroz Vukovar. Praćen je sadržaj fosfata kroz dvije godine (jesen, zima, proljeće i ljeto). Sadržaj fosfata u Dunavu kod Vukovara je promjenjiv.

Na sadržaj fosfata mogu utjecati: industrija, poljoprivreda, kućanstva kao i raspadanje uginulih biljka i životinja.

4. Susret mladih kemičara / 4th Meeting of young chemists

Obradiva tla u okolici grada Vukovara

Fertile soil in the Vukovar region

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Tlo je, poput vode i zraka, ključna sastavnica okoliša. Ubraja se u uvjetno obnovljive resurse s obzirom na dugotrajne procese nastanka i razvoja. Zemljište je nastalo kao rezultat dugotrajnih procesa promjene matičnog supstrata. Sadrži produkte raspadanja stijena te biljnih i životinjskih organizama. Međusobnim djelovanjem mineralnih i organskih tvari uz neposredno sudjelovanje živih organizama stvara se složeni kompleks zemljišnih spojeva. Tlo je temelj za proizvodnju hrane, organskih tvari, spremišta hranjiva za biljke i oborinske vode. Ono djeluje kao filter, pufer, obnavlja i čisti podzemnu pitku vodu. Nasuprot dugotrajnom procesu nastajanja, proces onečišćenja i oštećenja tla, posebice pod utjecajem čovjeka, neusporedivo je brži. U želji za povećanom proizvodnosti tla iz godine u godinu obradivim površinama dodaju se velike količine mineralnih gnojiva. Nakon nekoliko uspješnih žetvi proizvodnja počinje opadati.

Slavonija je hrvatska žitnica, a Vukovar grad okružen obradivim površinama.

Ispitana su obradiva tla u okolici grada Vukovara, prije sjetve pomoću seta za analizu tla. Iz ekstrakta tla određen je sadržaj NO_2^- , NO_3^- , NH_4^+ , P, K i pH vrijednost, sadržaj CO_3^- određen je gravimetrijski.

Tla spadaju u slabo kisela, u tlu dušik je zastupljen u obliku NO_3^- iona, sva tla imaju vrlo nizak sadržaj fosfora, opskrbljenost tla kalijem je dobra, sadržaj karbonata varira ovisno o uzorku.

Kiselost gaziranih sokova i utjecaj na čovjeka

Acidity of gasified drinks and its influence on man

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Konzumiranje bezalkoholnih pića uključujući gazirana pića, voćne sokove i sportska pića, u posljednjih je 50-ak godina u stalnom povećanju i ovaj trend ne pokazuje znakove zaustavljanja. Kontinuirano povećavanje konzumacije bezalkoholnih pića kod adolescenata izaziva zabrinutost kod posljedica na zdravlje. Bezalkoholna pića su slatka, aromatizirana, zakiseljena, obojana, a mogu sadržavati ugljični dioksid i konzervanse. Potrošnja u Hrvatskoj stalno raste. Prosječna potrošnja po glavi stanovnika je 62 litre godišnje ili 0,17 l dnevno.

Zdravo čovjekovo tijelo je slabo alkalno tj. $\text{pH} \sim 7,365$. Kada se u organizmu poremeti kiselo-bazna ravnoteža tijelo nastoji to popraviti. Pitka voda u većini zemalja je neutralna ($\text{pH} \sim 7,0$), a gazirana pića imaju $\text{pH} \sim 2,5$. U medicini je dobro poznato da se bolesti razvijaju u kiseloj sredini (virusi i bakterije te kancerogene stanice). Sadržaj fosfatne kiseline u bezalkoholnim pićima može reducirati apsorpciju kalcija i doprinijeti osteoporozi.

Praćena je kiselost gaziranih bezalkoholnih sokova mjerenjem pH vrijednosti pomoću pH- metra. Ustanovljeno je da se pH vrijednost ispitanih gaziranih sokova kreće od 2,44 do 3,38. Poznatom volumenu gaziranih sokova dodavana je pitka voda ($\text{pH} = 7,12$) pomoću birete i mjerena promjena pH vrijednosti. Voda je dodavana sve dok uzorak nije postao neutralan $\text{pH} = 7$. Određeno je kako za neutralizaciju jedne čaše gaziranog bezalkoholnog pića potrebno je od 15,8 do 26,8 čaša vodovodne vode.

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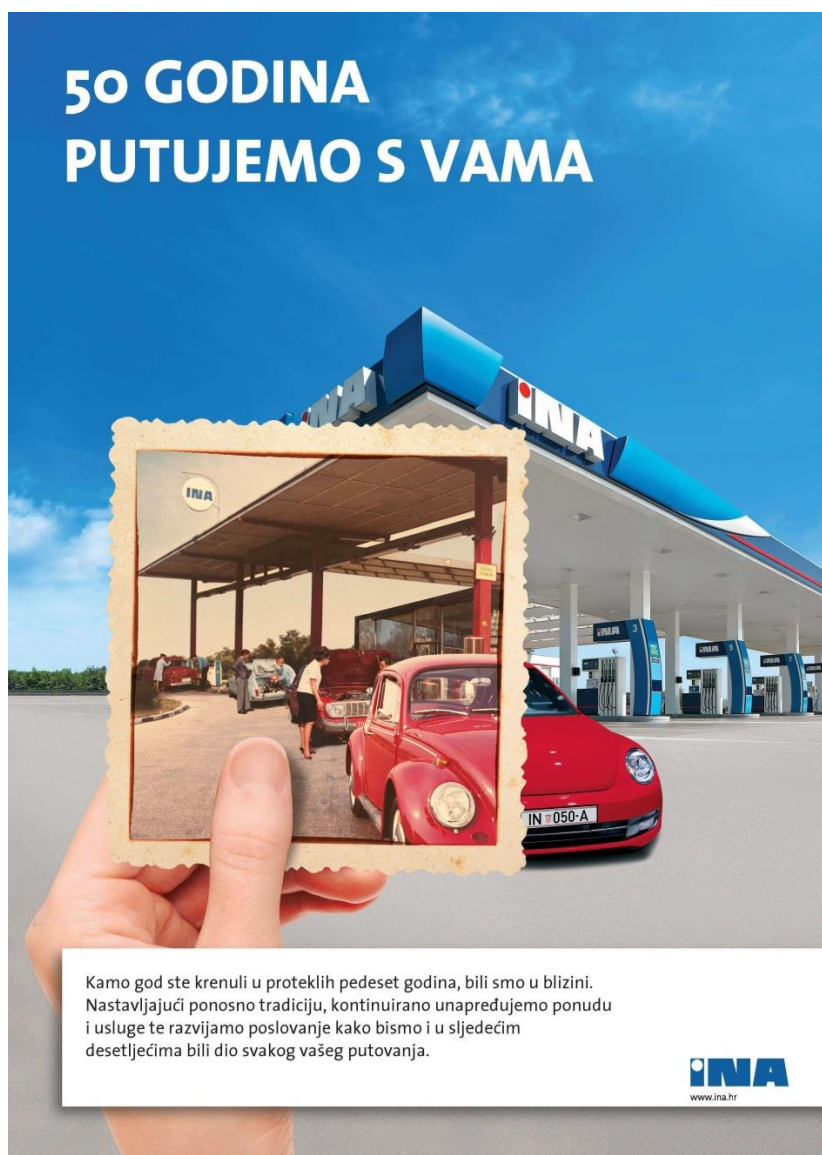
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The advertisement features a large, modern INA gas station with blue and white branding under a clear blue sky. In the foreground, a hand holds a vintage, scalloped-edge photograph. The photo shows a classic red Volkswagen Beetle parked at an older, simpler gas station with a canopy. A person is standing near the car in the photo. The text '50 GODINA PUTUJEMO S VAMA' is prominently displayed in white on the blue background of the top left. Below the photo, a white box contains text in Croatian, and the INA logo with the website 'www.ina.hr' is in the bottom right corner.

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i usluge te razvijamo poslovanje kako bismo i u sljedećim
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