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XIV. RUŽIČKINI DANI

Uvodna riječ

Ante Jukić

Predsjednik znanstveno-organizacijskog odbora

Znanstveno-stručni skup *14. Ružičkini dani* održava se u Vukovaru od 13. do 15. rujna 2012. godine. Od prethodnog skupa, *13. Ružičkinih dana*, održanog 2010. godine, poprima međunarodni karakter, a uz Hrvatsko društvo kemijskih inženjera i tehnologa (HDKI) i Prehrambeno-tehnološki fakultet Sveučilišta Josipa Jurja Strossmayera u Osijeku (PTFOS) ovogodišnji suorganizatori su i European Federation of Food Science and Technology (EFFoST) i European Association for Chemical and Molecular Sciences (EuChemS). Predsjednici ovih udruga, prof. dr. sc. Dietrich Knorr, i prof. dr. sc. Ulrich Schubert, pozdravit će Skup i kao vrsni stručnjaci održati i plenarna predavanja u svojim područjima. Glavna svrha *Ružičkinih dana* predstavljanje je znanstvene i stručne djelatnosti iz područja kemije, kemijskog i biokemijskog inženjerstva, prehrambene tehnologije, biotehnologije, medicinske biokemije i farmacije, te kemije u poljoprivredi, šumarstvu i zaštiti okoliša. Ciljevi su promicanje izvrsnosti, interdisciplinarnosti, originalnosti i inovativnosti u znanstvenim istraživanjima kao i primjena istraživanja kroz suradnju s gospodarstvom, a time i poboljšanje konkurentnosti te opći razvitak društva. Ove težnje vidljive su i kroz slogan "DANAS ZNANOST - SUTRA INDUSTRIJA". Stoga smo posebno zadovoljni činjenicom da su uz veliki broj radova sudionika s fakulteta i instituta u značajnom broju zastupljeni i raznovrsni radovi naših kolega iz industrije. Time se želi i nudi mogućnost poticanja rasprave kao i uspostave suradnje među sudionicima iz visokih učilišta, instituta i gospodarstva, budući da je svaki skup ujedno i prigoda susreta, razmjene mišljenja i iskustava. Uz plenarna, odabrana usmena i posterska priopćenja, susret mladih kemičara, u okviru Skupa predstaviti će se i raspraviti nova strategija i akcijski plan Europske komisije "*Inovacije za održivi rast: bioekonomija za Europu*". Sadržaj Skupa upotpunjuju i društvena događanja – prijem dobrodošlice i svečana večera, izlet koji će obuhvatiti obilazak vukovarske vojarne, Iločkih podruma s degustacijom vina, Muzeja grada Iloka u obnovljenom dvorcu Odescalchi, kao i izložbe u gradu Vukovaru.

Od svojih početaka, osim u ratno vrijeme, Ružičkini dani se održavaju u Vukovaru u sjećanje na nobelovca Leopolda (Lavoslava) Ružičku, rođenog u ovom hrvatskom gradu prepoznatljive i neizbrisive tradicije i značenja. Povodom 125. godišnjice njegova rođenja, 13. rujna 1887., kolege S. Tomas, M. Planinić, A. Bucić-Kojić, N. Pavić i I. Hubalek napisali su prilog "*Nobelovac Ružička kao izvor nadahnuća*", koji će biti predstavljen i uvodnim predavanjem.

Na ovogodišnjem skupu prijavljeno je više od 140 radova od gotovo 400 autora. Svim sudionicima u ime Znanstveno-organizacijskog odbora želim ugodno druženje i plodonosan rad tijekom skupa! Također, srdačno zahvaljujemo pokroviteljima, svim podupirateljima i donatorima, članovima Počasnog odbora i svima koji su pomogli i doprinijeli održavanju *14. Ružičkinih dana*!

NOBELOVAC RUŽIČKA KAO IZVOR NADAHNUĆA (Povodom 125. godišnjice njegova rođenja, 13. rujna 1887.) NOBEL LAUREATE RUŽIČKA - A SOURCE OF INSPIRATION

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Sir Isaac Newton svojedobno je rekao: „Vidio sam dalje od drugih zato što sam stajao na ramenima divova“. Istaknuti svjetski znanstvenici spadaju među te divove, pa tako i prvi hrvatski nobelovac, Leopold (Lavoslav) Ružička, rođen u Vukovaru, 13. rujna 1887., a umro u Mammernu (Švicarska) 26. rujna 1976. On je plamtio, kako je za znanstvenike napisao Jon Balchin u svojoj knjizi *100 znanstvenika koji su promijenili svijet* [1], rečeno poetskim riječima Bertranda Russela „podnevnim blještavilom ljudskoga genija“. Kao što je poznato, Nobelovu nagradu za kemiju dobio je za 1939. godinu pa je osobito od tada, premda je toga bilo i prije, omogućio mnogim suradnicima, dakako i onima koji su dolazili iz Hrvatske, da se „penju na njegova znanstveno divovska ramena“ i da pokušaju vidjeti dalje od drugih. Jedan među njima, Vladimir Prelog, i sam je ušao u krug takvih divova, jer je kao Ružičkin suradnik i nasljednik postigao takve rezultate, da je i sam dobio Nobelovu nagradu za kemiju za 1975. godinu.

Brojnim svjetskim i hrvatskim znanstvenicima Ružička je više ili manje, što direktno, što indirektno, bio i jest izvor nadahnuća. Akademik Trinajstić napisao je knjigu *100 hrvatskih kemičara* [2] u kojoj je dao kratke prikaze života i rada za 100 kemičara-kemijskih inženjera, po njemu najistaknutijih u dosadašnjoj hrvatskoj povijesti. Za njih 90 od ukupno 100 prikazanih, kao i za mnoge koji nisu uspjeli ući među te odabranike, gotovo se

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sa sigurnošću može reći kako im je prvi hrvatski nobelovac na neki način bio izvor nadahnuća i poticaja za njihov rad i djelatnost.

Dr. Jure Petričević u svome članku *Nobelovac prof. Leopold Ružička 80-godišnjak* [3] prenosi i komentira dijelove članka iz uglednog züriškog dnevnika *Neue Züricher Zeitung*, jutarnjeg izdanja od 13. rujna 1967. Radi se o feljtonu o Ružički, napisanom od Alberta Eschenmosera, koji citira sljedeće Ružičkine riječi: „Odrastao sam kao siroče u Hrvatskoj i bio sam vatreni patriot, zbog čega više nisam mogao podnijeti prilike u staroj austrijskoj carevini. Moj patriotizam, koji sam prenio na Švicarsku, ispoljio se na jedan trijezan ali koristan način: uložio sam svu snagu, da izobrazim dobre kemičare, koji će našoj industriji, dakle našoj zemlji, učiniti velike usluge.“ Te njegove riječi same za sebe dovoljno govore, jer ukazuju na to kako i jedno siroče, koje potječe iz europske periferije, može dosegnuti najveće uspjehe, te su poticajne svim ljudima, osobito mladima koji su u sustavu obrazovanja.

Osim Nobelove nagrade za kemiju, Ružička je dobio nagradu Švicarskoga kemijskog društva (1918.), Wernerovu nagradu i medalju Švicarskoga kemijskog društva (1923.), Le Blancovu medalju (uz počasno predavanje) Francuskoga kemijskog društva (1928.), Pedlerovu medalju (uz počasno predavanje) Engleskoga kemijskog društva (1931.), Medalju (uz počasno predavanje) Industrijskoga društva iz Mulhousea (1935.), Cannizzarovu nagradu Akademije Lincei (1936.), Lavoisierovu medalju (uz počasno predavanje) Francuskoga kemijskog društva (1937.), Nagradu Marcel-Benoist Švicarskoga kemijskog društva (1939.), Medalju (uz počasno predavanje) Sveučilišta u Liegeu (1940.), Nagradu Donegani Akademije Lincei (1948.), Faradayevu medalju (uz počasno predavanje) Engleskoga kemijskog društva (1958.) i Hanušovu medalju Čehoslovačkoga kemijskog društva (1966.). Ružička je također počasni član HAZU, a dodijeljen mu je i počasni doktorat osam svjetskih sveučilišta, te je bio članom petnaestak svjetskih akademija znanosti i počasnim članom tridesetak znanstvenih društava [4, 5]. Izložba *Znanost u Hrvata*, po kojoj se prikazalo dostignuća 16. velikana hrvatskog prirodoslovlja, obuhvatila je i nobelovce Ružičku i Preloga.

Brojne su manifestacije u Hrvatskoj kojima je nadahnuće bio Ružička. U Vukovaru je Ružički u spomen podignut muzej u njegovoj rodnoj kući, koji je otvoren 9. prosinca 1977. Hrvatsko kemijsko društvo utemeljilo je nagradu pod nazivom Nagrada Leopold Ružička za znanstvenike do 35 godina starosti. Nagrada koja se dodjeljuje iz kemije mladim znanstvenicima koji rade u Švicarskoj, nazvana je *Ružička*. U Vukovaru je osnovano veleučilište pod nazivom *Veleučilište Lavoslav Ružička*. Družba *Braća Hrvatskoga Zmaja - Zmajski stol u Osijeku* obilježila je uspomenu na istaknute učenike osječke gimnazije, Josipa Jurja Strossmayera (1815. - 1905.), Leopolda Ružičku (1887. – 1976.) i Vladimira Preloga (1906. – 1998.), postavljanjem njihovih poprsja na Rondel velikana osječke gimnazije, na ulazu u baroknu jezgru Tvrdū, pred zgradom današnje III. gimnazije, 29. siječnja 2007. XX. jubilarni hrvatski skup kemičara i kemijskih inženjera, koji se održao od 26. veljače do 1. ožujka 2007. u Zagrebu, bio je posvećen Leopoldu Ružički i Vladimiru Prelogu. Isto je tako *Zmajski stol u Vukovaru* izradio Rondel – spomenički prostor Lavoslava Leopolda Ružičke, s njegovim poprsjem, pred ulazom u zgradu vukovarskog veleučilišta, koje nosi njegovo ime, a otvoreno je 19. rujna 2008. Ružičkina kuća u Vukovaru, koja je bila devastirana tijekom agresije na Vukovar, obnovljena je, te je u dvorišnom prostoru izgrađena multimedijaska dvorana, u kojoj se održavaju brojne kulturne, znanstvene, stručne i zabavne manifestacije.

Ipak, možda su i najznačajnije manifestacije posvećene prvom hrvatskom nobelovcu Leopoldu Ružički znanstveni skupovi pod nazivom *Ružičkini dani*, koji se održavaju u Vukovaru, s tim da su *I. Ružičkini dani* održani 7. i 8. prosinca 1978., a do danas je održano ukupno četrnaest takvih skupova, od početka u organizaciji Hrvatskog društva kemijskih inženjera i tehnologa (HDKI).

Kolika je moć nadahnuća Ružičkinim životom i djelom, odnosno kolika je moć jedne dobre ideje, poput ove o održavanju *Ružičkinih dana* u Vukovaru, pokazuje i činjenica kako njihovo održavanje nije mogla obustaviti niti ratna agresija na Hrvatsku 1991. Istina, zbog agresije su *VII. Ružičkini dani* održani 1993. u Bizovačkim toplicama (umjesto 1991. u Vukovaru), gdje su održani i *VII. Ružičkini dani* 1996. Nakon mirne reintegracije Hrvatskog podunavlja, *Ružičkini dani* su se vratili kući i *IX.* su održani 1998. u Vukovaru, gdje su se nastavili održavati sve do danas, s dobrom perspektivom i za ubuduće [6].

Moć ove ideje potkrjepljuje i činjenica kako je od *XIII. Ružičkinih dana* skup postao međunarodni kongres, jer je suorganizator postala European Federation of Food Science and Technology (EFFoST). U prilog tome idu i podatci kako je na dosadašnjih četrnaest *Ružičkinih dana* održano preko 100 plenarnih predavanja, 130 ostalih predavanja, 550 priopćenja na posterima i pet okruglih stolova, od strane nobelovaca, akademika, sveučilišnih profesora, znanstvenika i inženjera iz zemlje i inozemstva. Skupove su organizirali znanstveni i stručni odbori, s ukupno 310 članova, a sveukupno je bilo oko 2300 sudionika iz domovine i inozemstva. Sve je to bilo i ostalo poticaj za razvoj gospodarstva i društva općenito, posebice na području kemije, kemijskog i biokemijskog inženjerstva, prehrambene tehnologije, medicinske biokemije, farmacije, zaštite okoliša i slično, u Hrvatskoj, ali i u svijetu. To je moć znanja koja djeluje kroz nadahnuća velikanima znanosti i duha, kakav je bio Ružička.

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PLENARNA IZLAGANJA

PLENARY LECTURES

EMERGING FOOD PROCESSING TECHNOLOGIES: FROM SCIENCE TO APPLICATIONS

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The food sector share of R&D investments is only 1 % and business expenditure on R&D as percentage of total output is 0.24 %. Consequently, radical changes in the policies related to research, development and innovation in the food sector is needed.

Emerging technologies such as high hydrostatic pressure, application of pulsed electric fields, cold plasma or ultrasound as well as combination processes allow new approaches for preservation and modification of foods. Understanding the relationships between processes, resulting food structures and subsequent properties provide a powerful toolbox for producing tailor made foods via targeted processing.

Examples will also be given on the development of high pressure and pulsed electric field technologies from a laboratory scale to industrial applications. In addition, possibilities for future industrial applications and process integration using emerging technologies will be provided.

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NEW SOL-GEL MATERIALS: FROM THE LABORATORY TO APPLICATIONS

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Sol-gel materials are prepared by controlled hydrolysis and condensation of hydrolyzable molecular precursors, such as metal or semi-metal alkoxides. One of the many advantages of sol-gel materials is the possibility to prepare inorganic-organic hybrid materials (materials consisting of inorganic and organic building blocks), which combine the properties of inorganic and inorganic materials. Other advantages are the mild synthesis conditions, the possibility to tailor composition, microstructure and porosity, and to prepare composite materials.

The aim of this contribution is to show how new precursor concepts, such as organically modified metal alkoxides with functional organic groups or bimetallic precursors with bridging by organic groups, can lead to new types of sol-gel materials. Examples for the latter will include multi-functional dense or porous coatings, nanostructured materials and nanocomposites, where nanoparticles are embedded in an oxide matrix.

THE APPLICATION OF MICROREACTORS IN BIOCHEMICAL ENGINEERING

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Nowadays, microreactors are finding more and more applications in many fields, from chemical industry and biotechnology to pharmaceutical industry and medicine. They offer many fundamental and practical advantages comparing to classical macroreactors such as large surface to volume ratio, excellent mass and heat transfer, shorter retention time, smaller amount of reagents, catalysts and waste products, laminar flow, etc. Microreactors consist of a network of micro-sized channels etched into solid substrate while typical dimensions of microchannels are in the range from 10 μm to 500 μm . They are connected to a series of reservoirs for chemical reagents and products to form a complete device called “chip”. Using microreactors, the complex scale-up procedure is replaced with numbering-up (replication of microreactor units), eliminating time and costs necessary for technology transfer from laboratory to industrial production. One of the biggest advantage of numbering-up is that continuous operation is uninterrupted if one of the units fails, because it can be easily replaced with no effect on other parallel units. Microreactors could be easily coupled with numerous detection techniques together with the pretreatment of the samples on the one single unit. Having in mind all those benefits one of the main motivations for the use of microreactor technology is the gain in the yield and safety.

The environmentally friendly and efficient development of products and processes is crucial for a sustainable development. An ecological and economic evaluation from the very beginning of the product/process design is therefore matter of prime importance. Evaluation procedure has to deal with a lack of knowledge in the early stages of product/process design and have to deliver sound results in the relatively short time period. It is possible to overcome that contradiction by using chemical engineering methodology that includes modeling, simulation and optimization of processes and process parameters. Modeling, simulation and optimization in combination with experiments performed in microreactors enable to take maximal advantage of the experimental data at disposition.

Microreactor advantages and chemical engineering methodology will be demonstrated on selected biotransformation and bioseparation processes, namely, alcohol dehydrogenase catalyzed hexanal production, NAD^+ cofactor regeneration catalyzed by enzyme, laccase catalyzed L-DOPA and catechol oxidations and two-phase aqueous extraction of polyphenols.

KVALITETA TJESTENINE OBOGAĆENE RAZLIČITIM FUNKCIONALNIM SASTOJJCIMA QUALITY OF PASTA ENRICHED WITH DIFFERENT FUNCTIONAL INGREDIENTS

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Pasta is recognized as one of the foodstuffs suited to a modern diet providing human organism with carbohydrates and protein. Growing awareness of the beneficial effects of a healthy diet on the quality of life has lead to developing of food products with special health-enhancing attributes (functional food). The pasta quality is defined by the means of the type of durum wheat from which the flour is produced, characteristics of the flour, the manufacturing processes, possible added ingredients and hygiene and preservation. Development of pasta as a functional food by incorporation of functional ingredients containing in soy, maize, extruded maize and barley flour was investigated. The most important criteria of dry pasta quality: external appearance (colour, spots, air bubbles, and smoothness) and other parameter of sensory quality after cooking (optimum cooking time, volume increase and cooking loss) were evaluated. The results showed that addition up to 25 % maize, 20 % extruded maize, 20 % soy and up to 40 % barley flours provides good quality pasta with enhanced functional properties.

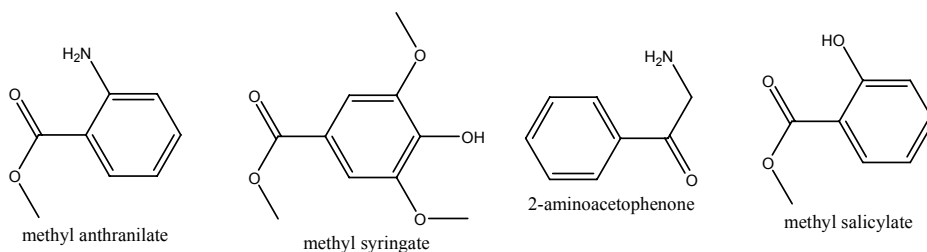
BIOORGANIC RESEARCHES: PHYTOCHEMICALS AS MARKERS OF HONEY BOTANICAL ORIGIN

Igor Jerković

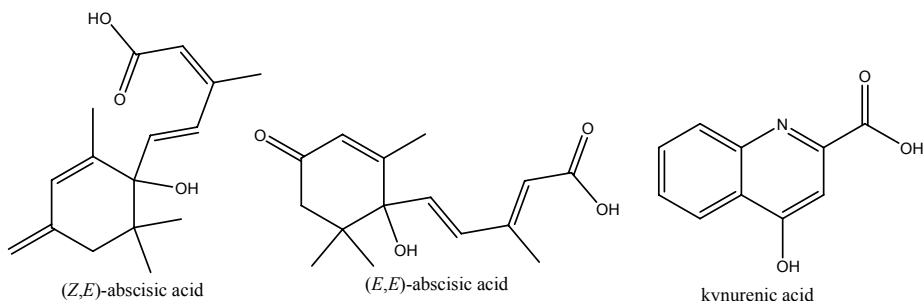
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The search for reliable chemical biomarkers and/or typical chemical profiles indicating floral or geographical origin of different honey types has been the focus of many studies in last 15 years with the scope of honey authenticity (encouraged by EU Council directive 2001/110/EC and Codex Alimentarius Standard). A number of phytochemicals has been identified (volatile organic compounds, phenolics, carbohydrates, nitrogen containing compounds and others) for botanical origin assessment, particularly important for honeydews characterization because mellisopalynological analysis cannot be carried out. It is now recognized that many phytochemicals can have health-promoting activities (such as antioxidant and/or antimicrobial activity). Nowadays, more than 600 volatile organic compounds (VOCs) have been identified in honeys of different floral origins contributing to the varieties of honey aroma. Honey VOCs are present at low concentrations as more or less complex mixtures of compounds with different organic functionalities. Due to high concentration of carbohydrates, special treatment of honey is required for VOCs isolation without artefacts formation (such as Maillard reaction and/or Strecker degradation products). The most frequently used isolation methods are ultrasonic solvent extraction (USE) and headspace solid-phase microextraction (HS-SPME) with a varying degree of selectivity and effectiveness depending on the compounds involved followed by gas chromatography and mass spectrometry analyses (GC-FID, GC-MS). Five sources of honey volatile organic compounds (VOCs) have been considered: 1) plant constituents (phytochemicals), 2) phytochemicals transformation by the bees, 3) direct compounds generation by the bees or compounds transfer from the combs environment, 4) their generation by honey thermal processing and 5) microbial or environmental contaminants. To determine the immediate contribution of the bees and combs to honey volatiles (blank-trial probe), the bees were closed in a hive containing empty combs under controlled food-flow conditions and the obtained "saccharose honey" was analyzed and higher alcohols with saturated linear long-chain hydrocarbons were identified (related to the composition of combs and cuticular waxes and less to the bee pheromones). Only few types of honey contain one characteristic specific compound, while the majority was characterized by several compounds (terpenes, norisoprenoids, shikimic acid derivatives and others). Several specific-marker volatile compounds have been suggested, e.g., methyl anthranilate for *Citrus* spp. honeys and 2-aminoacetophenone for *Castanea sativa* honey. Other biomarker compounds were methyl syringate for *Asphodelus microcarpus* Salzm. et Viv. honey or methyl salicylate for *Salix* spp. honey and others. Coumarin and vomifoliol were reported as nonspecific biomarkers of *Prunus mahaleb* L. honey.



To find specific or nonspecific phytochemicals in the honey different approaches are available such as the analysis of nectar or bee-stomach content. Comparison of *Mentha* ssp. honey organic extractives with the corresponding bee-stomach extractive indicated that methyl syringate and vomofoliol were transferred to the honey while terpendiol I was partially transformed to hotrienol in ripened honey. *Salvia officinalis* L. honey contained lumichrome that was also identified (HPLC-DAD; HPLC-MS) in the corresponding bee-stomach. Asphodel honey contained on average about 80% of the original methyl syringate found by HPLC-DAD in the nectar taken from asphodel flowers. Found specific or nonspecific phytochemicals can be also very useful for characterization of honey-based products, such as *abbamele* (a typical Sardinian product obtained from the honey recuperation from combs or by concentration of the honey diluted in water). GC-MS analyses of *abbamele* USE isolates revealed the honey marker compounds such as methyl syringate, biomarker of asphodel honey. High isophorone percentage determined by HS-SPME followed by minor percentage of 4-ketoisophorone and norisoprenoids indicated *Arbutus unedo* L. honey use in *abbamele* production. HPLC-DAD analysis confirmed the presence of specific honey markers: high methyl syringate concentrations (characteristic for asphodel honey) and homogentisic acid with other specific markers of *A. unedo* honey were found. In addition, phytochemical research by direct HPLC-DAD method can be used for distinguishing nectar and honeydew honey from the same natural source. For example, abscisic acids (ABA) are typical of willow nectar honey, with a predominance of (*Z,E*)-ABA on (*E,E*)-ABA. Kynurenic acid and salicylic acid were useful to mark willow honeydew honey.



NEW BIOTECHNOLOGICAL PRODUCTS – RESEARCH AND INDUSTRY

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Biotechnological research and manufacture are currently focused on the production of fine chemicals, biofuels, biopolymers, different functional food products as well as on the environment protection. In order to achieve sustainability of these bioprocesses life cycle analysis (LCA) has to be performed and it should result in the improvement of bioprocess performance. In this work, overview of previously mentioned bioprocesses will be made. Industrial production of bioethanol (as a biofuel) is currently based on the sugar and polysaccharides containing raw materials, but intensive research is performed on the lignocellulosic raw materials. Many companies and research institutions are working on the production of fine chemicals and one example of these products is β - glucan that could be produced by algae *Euglena gracilis*. Biopolymers production and their sustainability also attract a lot of interest of companies and institutions and good examples are production of polylactic acid (PLA) and polyhydroxyalkanoates (PHA). Food companies and institutions continuously work on the improvement of the quality of different functional food products. Bioprocess engineers are working on new bioreactor constructions (especially for bioprocesses on the semi-solid and solid substrates) for different bioprocesses in order to improve the bioprocess performance. Heavy metals removal process is a good example of research in the field of environment protection.

USMENA PRIOPĆENJA
ORAL PRESENTATIONS

COVALENT FUNCTIONALIZATION OF MWCNT FOR BETTER DISPERSION IN POLYMER MATRICES

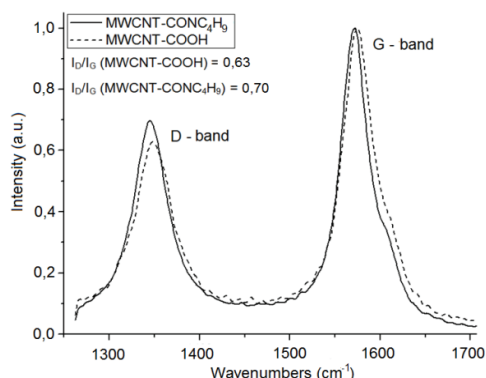
KOVALENTNA FUNKCIONALIZACIJA UGLJIKOVIH NANOCIJEVI RADI POSTIZANJA BOLJE RASPODJELE U POLIMERNIM MATRICAMA

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Because of their unique structure and physical properties carbon nanotubes draw a lot of attention. Properties like large interfacial contact area, high stiffness and strength, great thermal and electrical conductivity, high aspect ratio and low mass density make them ideal reinforcement fillers. However, due to the Van der Waals interactions it is very challenging to prevent the agglomeration of carbon nanotubes in bundles. That's why an appropriate chemical treatment of the nanotube surface is required for a fine dispersion to be accomplished. Another reason for their surface functionalization is achieving better or specific interaction between carbon nanotubes and polymer matrix. In this work covalent modification of multiwall carbon nanotubes (MWCNT) was performed which has enabled introduction of new alkyl ending on carbon nanotube surface by ester or amide linkage. Modified MWCNT were characterized by spectroscopic and thermal methods.



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ODREĐIVANJE ANIONIJSKIH TENZIDA SEKVENCIJALNOM INJEKCIJSKOM ANALIZOM ANIONIC SURFACTANT DETERMINATION USING SEQUENTIAL INJECTION ANALYSIS

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Sequential Injection Analysis (SIA), was employed in the investigations reported for determination of anionic surfactants (AS) in the solution of detergent formulations [1,2]. A potentiometric flow through self-made sensor was used as a detector using 1,3-didecyl-2-methylimidazolium-tetraphenylborate ion-pair as a sensing material [3]. The solutions of sodium dodecyl sulfate and sodium dodecylbenzenesulfonate were used for the calibration of the system. The detector responded linearly to the logarithmic changes of the surfactant ion activities with the detection limit below 1 μM of AS investigated. Sample and reagent injection as the initial input parameters were investigated and optimized. A particular attention was paid to the selection of the carrier, controlling of dispersion process as well as to the reproducible timing. The standard addition method was used for testing the accuracy of the SIA determination, whereas the potentiometric titration was used as a reference one [4].

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**UTJECAJ KARAKTERISTIKA CJEPIVA NA
GRANULOMETRIJSKA SVOJSTVA KRISTALA
BORAKSA U PROCESU ŠARŽNE KRISTALIZACIJE
SEED PROPERTIES EFFECT ON GRANULOMETRIC
CHARACTERISTICS OF BORAX IN BATCH COOLING
CRYSTALLIZATION**

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In this work the influence of seed surface area and shape factor on granulometric properties of disodium tetraborate decahydrate (borax) obtained by batch cooling crystallization were investigated. In the crystallizer with the volume of 2.14 dm^3 , mixing was performed by straight blade turbine impeller (abbrev. *SBT*). In all experiments impeller speed was kept constant ($N = 350 \text{ rpm}$) in order to ensure the state of complete suspension in the system. Mother liquor, saturated at temperature of $30 \text{ }^\circ\text{C}$, was cooled down at rate of $6 \text{ }^\circ\text{C h}^{-1}$.

In the first part of the work, unseeded batch cooling crystallization was carried out in order to determine the metastable zone width, granulometric properties of crystal product and to define conditions under which seeded crystallization will be performed. Afterwards, the influence of seed surface area and shape factor on the crystal size distribution and agglomeration ratio of final product was investigated. Crystals of borax with needle and plate-like morphology, in the size range from 45 to $142 \text{ }\mu\text{m}$, were used as a seed. In order to examine the effect of seed surface area, different masses of crystals of defined size and shape factor were added to the mother liquor. The analysis of crystal size distribution and agglomeration ratio of final crystal product obtained for each examined seed surface area was carried out. The obtained data were examined in details. The seed that results in borax crystal product with a narrower crystal size distribution, larger weight mean diameter and lower agglomeration ratio, could be considered as optimal option.

PRAKTIČNI UVID U RAZVOJ MODELA FILTRACIJE I CENTRIFUGIRANJA PRACTICAL INSIGHT IN THE DEVELOPMENT OF A FILTRATION AND CENTRIFUGATION MODEL

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Proizvodnja aktivnih farmaceutskih sastojaka (API-ja) i njihovih intermedijera kao krutih proizvoda najčešće se sastoji od procesa kristalizacije, filtriranja i sušenja. U nekim slučajevima, filtriranje API-ja i/ili njihovih intermedijera može pokazati duge cikluse i može biti usko grlo cijelog procesa. Stoga je određivanje svojstava filtarskog kolača potrebno za procjenu filtriranja prije uvećanja procesa (*scale up*). Korištenjem tlačne filtarske cijevi i procjenom parametara određuju se otpornost i stlačivost filtarskog kolača na temelju eksperimentalnih podataka [1]. Simulacijom procesa centrifugiranja na osnovi prethodno određenih parametara mogu se predvidjeti sve bitne značajke filtracije [2]. Optimiranjem procesa metodologijom određivanja procesnog prostora (*space design*) može se odrediti optimalno područje parametara filtriranja, te robusnost samog procesa i ključni parametri (vrijeme punjenja i brzina vrtnje centrifuge). Rezultati studija slučaja (*case study*) pokazuju da kombiniranje ova dva pristupa može biti prikladno za predviđanja performansi filtracije u pilotu i proizvodnom pogonu.

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ANALIZA OSJETLJIVOSTI PARAMETARA CBC- MODELA BIOREMEDIJACIJE BTEX-a PARAMETER SENSITIVITY ANALYSIS OF CBC MODEL OF BTEX BIOREMEDIATION

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Benzene, toluene, ethylbenzene and xylene belong to a group of monoaromatic organic compounds (BTEX). Due to their great mobility in the environment, their presence in natural waters and soils is a serious environmental problem. Bioremediation of BTEX primarily relates to the biological activity of microorganisms in soil and water [1], [2]. For the purpose of better understanding the complex chemical and biochemical processes that occur during BTEX degradation, a Coupled Biological and Chemical Model (CBC) was developed which includes the basic microbiological and chemical reactions that affect the presence and the concentration of intermediates [3]. In this research, the analysis of coupled CBC model for BTEX bioremediation was performed. The kinetic model describes the microbial BTEX degradation, decay of biomass, methanogenesis, and oxidation of the organic fermentation products. Model contains 16 differential equations and 54 kinetic parameters and suggests that the time change of each metabolite concentration is a difference between the rate of formation and consumption of individual molecules. The aim of this research was to determine the key parameters of CBC model for BTEX bioremediation by applying FAST (Fourier Amplitude Sensitivity Test) method. FAST algorithm provides sensitivity on high and simultaneous changes in the overall set of model parameters. The obtained results indicate the key points of bioremediation process and enable planning of the future experiments.

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OČVRŠĆIVANJE NEZASIĆENIH POLIESTERSKIH SMOLA U KALUPIMA CURING OF UNSATURATED POLYESTER RESINS IN MOULDS

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U ovome radu analiziran je prijenos topline i kinetika reakcije očvršćivanja nezasićenih poliesterskih smola sa i bez punila grijanjem bakrenog kalupa vrućim zrakom i uljem. Kinetika reakcije očvršćivanja određena je diferencijalnom pretražnom kalorimetrijom (DSC), a prijenos topline kroz kalup mjerenjem temperature u središtu uzorka te iz vanjsku stjenku kalupa. Provedena su mjerenja kojima se istražuje vođenje topline kroz uzorak u kojem se odvija reakcija. Na istim temperaturama zračne kupelji istražen je i utjecaj punila na proces očvršćivanja. Reakcijska smjesa je sadržavala smolu, inicijator i punilo. Tijekom eksperimenta korištene su četiri komercijalne smole dobavljene od Scott Bader, Hrvatska, koje do sada nisu bile korištene u sličnim eksperimentima proteklih godina. Izveden je matematički model reakcije očvršćivanja koji se sastoji od sustava parcijalnih diferencijalnih jednadžbi, koje opisuju bilancu tvari i topline kao i reaktorski model za kotlasti reaktor i kinetički model autokatalitičke reakcije. Prijenos topline sa zraka na stjenku kalupa odigrava se konvekcijom, a kroz uzorak unutar kalupa vođenjem što je definirano u modelu kroz rubne uvijete i bilancu topline. Predloženi model riješen je uz definirane rubne uvjete numeričkom metodom linija za rješavanje sustava PDJ uz istovremenu procjenu parametara modela (ID algoritam). Na temelju provedenih eksperimenata u kalupu i provedene matematičke analize dobivena je potpunija slika reakcije očvršćivanja u modelnim kalupima, a stečene spoznaje mogu se primijeniti pri izradi konstrukcijskih materijala na bazi nezasićenih poliesterskih smola kao i pri modeliranju proizvodnih kalupa.

UZGOJ *PSEUDOMONAS PUTIDA* U RAZLIČITIM TIPOVIMA REAKTORA CULTIVATION OF *PSEUDOMONAS PUTIDA* IN DIFFERENT CONFIGURATIONS OF BIOREACTORS

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Pseudomonas putida is an industrially very interesting microorganism with an ability to degrade numerous toxic compounds. Because of that, this gram-negative rod shaped bacteria has a big potential for long term solution of environmental problems caused by toxic compounds as a result of their use in agriculture and other fields. It is very adaptable to different growth conditions and characterized by a big metabolic enzyme portfolio.

In this work, *Pseudomonas putida* strains KT2440 and VLB120ΔC were cultivated in a batch, fed-batch and continuous reactor. During batch cultivation, the influence of two different growth media, M9 and M12, for microorganism cultivation were investigated by experiments with both strains. Better results were achieved in experiments with starting concentration of glucose $\gamma = 15 \text{ g dm}^{-3}$ by cultivating bacteria on M12. For strain VLB120ΔC the highest specific growth rate of $\mu = 0.837 \text{ h}^{-1}$ was recorded with final maximum biomass concentration of $c_X = 11.58 \text{ g dm}^{-3}$. Same medium was used in fed-batch experiments where the highest growth rate of $\mu = 0.599 \text{ h}^{-1}$ and maximum biomass concentration of $c_X = 11.98 \text{ g dm}^{-3}$ were achieved in experiment with specific glucose feed rate of $9.5 \text{ g h}^{-1} \text{ dm}^{-3}$. In experiments performed in continuous reactor for different retention times, M12 growth media with 15 g dm^{-3} glucose was used as inlet stream. The experiment was carried out for 5 days and maximum biomass concentration of $c_X = 7.50 \text{ g dm}^{-3}$ was achieved for retention time of $\tau = 20 \text{ h}$. Based on current research efforts, the batch reactor is shown to be the best reactor configuration for *Pseudomonas putida* cultivation if reactors were evaluated by the highest specific growth rate achieved.

TREATMENT OF SUGAR BEET WASTE IN SOLID-STATE OPERATING BIOREACTOR

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Solid-state fermentation (SSF) is a process performed in the absence of free water on non-soluble materials which can act as physical support and source of nutrients to microorganisms [1]. In this paper white rot fungus *Trametes versicolor* was cultivated in aerated solid state-operating bioreactor with the air inlet flow of 3 L min⁻¹ kg⁻¹ using sugar beet waste as a substrate. The main objective of the work was to determine the lignin-degrading capacity and TC removal capacity of the applied fungus. The initial material was comprised of 4.82 % of lignin, 21.5 % of cellulose and 43.79 % of total carbon (TC), out of which 0.01 % inorganic carbon (IC) and 43.78 % organic carbon (TOC). In comparison to lignin degradation, where 69 % of lignin was degraded, cellulose was not degraded. The results of TOC analysis confirmed this fact, while TC degradation capacity was only 1 %.

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EFFECT OF TREHALOSE AND SUCROSE ADDITION ON PHENOLS, ANTIOXIDANT ACTIVITY AND COLOUR IN APPLE JUICE

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The objective of this study was to investigate influence of trehalose and sucrose addition (10 %) on phenol content, antioxidant activity and colour in apple juice during storage at room temperature and at 4 °C. Apple juice was obtained from Golden Delicious, Pink Lady and Fuji varieties. Apple juice without sugar addition was used as control sample. The highest phenol content had juice from Pink Lady variety, than Fuji and Golden Delicious (828.25, 796.01 and 749.67 GAE mg/L, respectively). During storage, degradation of phenols occurred at both storage temperature, but in higher extent at room temperature. Addition of sugars had high influence on phenol content in comparison to control sample. Samples with addition of sucrose had lower, while samples with addition of trehalose had higher phenol content in contrast to control sample. DPPH and ABTS methods were used for antioxidant activity determination. The lowest antioxidant activity had juice from Pink Lady variety (5.82 and 8.48 µmol TE/100 mL obtained with DPPH and ABTS method). Juice from Fuji and Golden Delicious variety had similar values of antioxidant activity regardless of used method (~7.3 and ~10.2 µmol TE/100 mL obtained with DPPH and ABTS method). During storage, increase of antioxidant activity occurred. This is probably due to formation of Maillard reaction products and/or chemical oxidation of phenols which can lead to increase of antioxidant activity since it was found that partially oxidised phenols can demonstrate higher antioxidant activity than unoxidised phenols. Calculation of colour change during storage showed that higher colour change was observed in samples stored at room temperature. In all samples when trehalose was added lower colour change was observed.

Key words: apple juice, phenol content, antioxidant activity, colour, storage.

CHARACTERIZATION OF THE EFFECT OF ALCOHOL DEHYDROGENASE IN *ENTEROCOCCUS FAECALIS*

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Enterococcus faecalis as a part of lactic acid bacteria ferment sugars through different pathways, resulting in homo- or mixed acid fermentation. Based on our knowledge until know no study has been done in analyzing the effect of alcohol dehydrogenase in *Enterococcus faecalis*. In order to study more in depth about central energy metabolism and to get a better understanding on connection between genes and metabolites alcohol dehydrogenase mutants has been making. HPLC and GC have been used for metabolite analysis; DNA microarray and RT-PCR in transcriptome profiles. Result shows that with the lack of the ethanol the energy goes into the formate and acetoin. In transcriptome profiles the genes which they are related to the energy metabolism they are regulated. This results shows that alcohol dehydrogenase (EF0900) is the right gene in genome for producing the ethanol.

Key words: alcohol dehydrogenase, transcriptome, *Enterococcus faecalis*.

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OPTIMISATION OF BLUEBERRY VACUUM DRYING PROCESS OPTIMIRANJE PROCESA VAKUUM SUŠENJA BOROVNICE

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Drying in a vacuum is one of the drying methods in which moisture is removed from the food at reduced pressure and temperature. The objective of this research was to optimize the vacuum drying of blueberries in order to preserve health benefits phytochemicals using response surface methodology. The drying was performed in a new design of vacuum dryer equipment. Investigated range of temperature was 46 – 74 °C and of pressure 38 – 464 mbar. Total solids, total phenolics, vitamin C, antioxidant activity, anthocyanin content and total colour change were used as quality indicators of dried blueberries. Within the experimental range of studied variables, the optimum conditions of 60 °C and 100 mbar were established for vacuum drying of blueberries. Separate validation experiments were conducted at optimum conditions to verify predictions and adequacy of the second-order polynomial models. Under these optimal conditions, the predicted amount of total phenolics was 3.7 mgCAE/100dw, vitamin C 59.79 mg/100gdw, anthocyanin content 2746.33 mg/100gdw, IC₅₀ 0.031 mg/ml, total solids 89.5 and total colour change 88.83.

Keywords: blueberry, vacuum drying, response surface methodology, product quality

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**UTJECAJ SUŠENJA GROŽĐA NA AROMATSKE
KOMPONENTE MOŠTA SORTE PLAVAC MALI
INFLUENCE OF THE OFF-VINE DRYING OF GRAPE ON
THE AROMATIC COMPOUNDS IN MUST FROM
PLAVAC MALI CV.**

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The aim of this research was to investigate the influence of off-vine drying of the grapes of Plavac mali cv. on the aromatic compounds of must in the production of traditional dessert wine Prošek. The grapes selected (23.8° Brix, pH value 3.76) for the experiments were taken from the germplasm of the Institute for Adriatic Crops and Karst Reclamation, harvested in 2009. They were dried in a glasshouse for 15 days at 21 – 37 °C. The must obtained from the dried grapes had 35.7° Brix, pH value 3.87 and total acidity of 8.34 g/L. SPME-GC-MS analysis was used to determine the volatile compounds before and after drying. Total acidity increased 1.96-fold during the process of drying. As many as 35 volatile compounds were determined and quantified. Their relative concentration in the must from dried grapes increased, especially the concentration of terpenes. Among terpenes, the most prevalent were 4-terpineol, linalool, linalool oxide, and *cis*- and *trans*-limonene epoxide. Norisoprenoids are products of degradation of carotenoids, among which β -damascenone was found in musts. Among higher alcohols, 3-methyl-1-butanol is quantitatively most significant component. Apart from the effect of concentration due to evaporation, anaerobic metabolism can also influence the increase of the volatile compounds ratio.

Key words: aroma, off-vine dried grapes, must, Plavac mali

OBJEDINJENI UVJETA ZAŠTITE OKOLIŠA U PETROKEMIJI D.D. – OBVEZE I PLAN PROVEDBE

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Usklađivanje propisa RH s propisima EU provedeno je donošenjem Uredbe o postupku utvrđivanja objedinjenih uvjeta zaštite okoliša NN 114/08 u koju su ugrađene IPPC Direktive 96/61/EC i 2008/1/EC. Donesena Uredba je obvezala tvrtke iz Annexa I da provedu analizu stanja svojih proizvodnih procesa i izvrše ocjenu sukladnosti s Najbolje raspoloživim tehnikama (NTR). Nakon provedene analize Petrokemija d.d. tvornica gnojiva u Kutini je utvrdila 17 nesukladnosti za koje je izradila plan usklađivanja. Plan usklađivanja je prihvaćen od Europske komisije, a odnosi se na razdoblje 2009. – 2017. godina. Ukupna ulaganja za planirane projekte predviđena su u iznosu 350 mil. kuna. U razdoblju 2009. – 2011. godina realizirani su sljedeći projekti:

- Smanjenje emisije NOx plinova na postrojenju Dušična kiselina 1
- Smanjenje emisije amonijaka u zrak iz reaktorske linije postrojenja NPK 1
- Rekonstrukcija obrade procesnog kondenzata postrojenja KAN 1
- Povrat otpadne vode od pranja pješčanih filtara na Postrojenju za pripremu, distribuciju i obradu voda

Za ovu namjenu utrošeno je 25,4 mil. kn. Na postrojenju NPK 1 smanjena je emisija amonijaka u zrak s prosječnih 800 na < 100 mg/m³. Emisija NOx na postrojenju Dušična kiselina 1 smanjena je s prosječnih 450 na < 90 ppm. Koncentracija amonijakalnog dušika u procesnom kondenzatu postrojenja KAN 1 smanjena je s prosječnih 2.000 na < 500 mg/m³, a povrat otpadne vode od pranja pješčanih filtara iznosi 1,5 mil. m³/godinu. U razdoblju 2012.-2017. godina planiraju se realizirati preostali projekti od kojih navodimo one čija je realizacija već započela:

- Smanjenje emisije amonijaka u zrak iz postrojenja Urea 2
- Pranje plinova iz linije granulacije postrojenja NPK 1.
- Ugradnja sustava za smanjenje emisije N₂O na postrojenju Dušična kiselina 1
- Ugradnja sustava za smanjenje emisije N₂O i NOx na postrojenju Dušična kiselina 2
- Izdvajanje amonijaka i vodika iz otpadnog plina niskotlačnog dijela sinteze postrojenja Amonijak 2
- Rekonstrukcija sustava za stripiranje procesnog kondenzata postrojenja Amonijak 2
- Ugradnja plamenika sa smanjenom emisijom NOx plinova na postrojenju Amonijak 2 i Energana
- Izgradnja retencije otpadnih voda s pripadajućim postrojenjem za obradu otpadnih voda.

Bit će prikazani tehničko-tehnološki uvjeti provedbe ovih projekata s očekivanim rezultatima u području smanjenju utroška energije i zaštiti okoliša. Za ove namjene predviđena ulaganja iznose 267 mil. kuna. Njihovom realizacijom očekuje se zadovoljenje zahtjeva koji će biti propisani u tzv. Okolišnoj dozvoli u kojoj će biti ugrađeni objedinjeni uvjeti zaštite okoliša temeljeni na IPPC Direktivama.

POSTERSKA IZLAGANJA / POSTERS
RADOVI PO SEKCIJAMA / SECTIONS

KEMIJSKA ANALIZA I SINTEZA
CHEMICAL ANALYSIS AND SYNTHESIS

**MULTIELEMENTNA ANALIZA PRIRODNE
IZVORSKE MINERALNE VODE METODAMA AAS,
AES I HG-AAS
MULTIELEMENT ANALYSIS OF NATURAL WELL
WATER BY AAS, AES AND HG-AAS METHODS**

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This paper presents the results of multielement determination of natural well water from Palež well, Kiseljak. The determination has been carried out by means of atomic emission and absorption spectrometry, as well as atomic absorption spectrometry hyphenated with hydride generation (HG-AAS). For determination of each element the corresponding calibration curve has been prepared. A total of 13 elements have been covered; potassium, calcium and sodium by flame AES, while calcium also with flame AAS; selenium and arsenic by HG-AAS, and all other elements by AAS. The natural well water pH value has also been measured.

The main purpose of this analysis has been evaluation of composition of well water and comparison of the results with currently actual guidelines and recommendations. This is especially important regarding seasonal use of analysed well water for drinking.

Keywords: multielement analysis, analysis of metals, AAS, AES, HG-AAS

PRELIMINARY SCREENING OF RARE APPLE (*Malus domestica* Borkh.) HONEY VOLATILES BY ULTRASONIC SOLVENT EXTRACTION

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Apple honey is rare due to relatively small apple nectar yield and difficulty for honeybees to access it caused by flower structure as well as due to the great variety of other nectariferous plants blooming at the same time. Analyzed honey sample (*Malus domestica* Borkh.), with specific pleasant fruity taste and aroma, was collected during spring 2011 in apple orchards in south Poland. Volatile and semi volatile compounds of the honey were isolated by ultrasonic solvent extraction (USE) with the mixture of pentane and diethyl ether (1:2 v/v) - solvent A and dichloromethane - solvent B and analyzed by gas chromatography and mass spectrometry (GC-MS) on HP-5MS column. A variety of compounds was identified, mainly various shikimate pathway derivatives (solvent A; solvent B) such as: phenylacetic acid (22.2 %; 17.5 %), benzoic acid (9.4 %; 7.3 %), methyl syringate (4.5 %; 3.5 %), benzaldehyde (3.3 %; 2.7 %) and lower amount of others (2-phenylethanol, benzyl alcohol or vanillin). The presence of shikimate pathway derivatives was previously reported in the volatiles emitted by apple flowers (benzyl alcohol, benzaldehyde, 2-phenylethanol and vanillin [1]). High abundance of phenylacetic acid and benzoic acid was previously found in heather, thyme and salvia nectar honeys as well as in willow and oak honeydew honeys. Since the odour threshold of these compounds is low, they contribute greatly to aroma. Phenylacetic acid is described as fruity, sweet, sour and benzoic acid as sweet, honey-like, slightly bitter. Phenylacetic acid is a phytohormone, member of the auxin class that plays important role in plant growth and organogenesis [2]. Phenylacetic acid was also found to exert strong inhibitory effect against gram-negative and gram-positive bacteria. [3]. Another compounds with higher percentages found in apple honey were: terpendiol I (5.1 %; 5.4 %), vomifoliol (4-hydroxy-3,5,5-trimethyl-4-(3-oxo-1-butenyl)-2-cyclohexen-1-one) (4.2 %; 7.07 %), 1-hydroxylinalool (3.3 %; 3.7 %) and coumaran (2.2 %; n.d.). Further research is needed to confirm noticed pattern of the compounds of apple honey sample. Even minor compounds could contribute to its characterization together with shikimate pathway derivatives

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**Ru(III) KOMPLEKSI KAO POTENCIJALNI
ANTI-KANCEROGENI AGENSI
Ru(III) COMPLEXES AS POTENTIAL ANTICANCER
AGENTS**

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Metali i njihovi spojevi igraju važnu ulogu u medicinskoj anorganskoj kemiji. Razvoj ove nove naučne discipline započinje u drugoj polovini dvadesetog stoljeća, tačnije 1960. godine, otkrićem antitumorskih osobina cisplatin, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ [1]. Od tada je prisutan značajan razvoj i upotreba anorganskih antitumorskih lijekova, pri čemu posebno dobru perspektivu pokazuju kompleksni spojevi druge i treće grupe prijelaznih metala. Među njima istaknuto mjesto zauzima rutenij, budući da se različiti tipovi kompleksa rutenija aktivno proučavaju kao lijekovi na bazi metala, zbog njihove relativno niske toksičnosti, dobre selektivnosti i antimetastatskog djelovanja [2]. U ovom radu je dat pregled do sada sintetiziranih Ru(III) kompleksa, potencijalnih antikancerogenih agenasa, kao i onih koji su, kao antikancerogeni agensi, uspješno prošli neku od faza kliničkih ispitivanja.

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**VODLJIVOST AMONIJEVOG BROMIDA U SMJESI
2-BUTANOL (5 MAS. %) – VODA
CONDUCTIVITY OF AMMONIUM BROMIDE IN
2-BUTANOL (5 MASS. %) + WATER MIXTURE**

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Molar conductivity of the NH_4Br solutions in binary mixture of 2-butanol and water with 5 mass. % alcohol content was measured at five temperatures in the range from 15 °C to 35 °C. The limiting molar conductivity (Λ_0) and the ion-pair formation constant (K_A) were determined by the Lee-Wheaton [1] conductivity equation. Thermodynamic quantities, Gibbs energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), for the ion-association reaction were derived from the temperature dependence of K_A . The obtained thermodynamic quantities, together with Walden product, were compared with literature data for NH_4Br [2] in mixtures with 2-butanol mass fraction (w) 70, 80, 90 and 95 %.

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SPECTROPHOTOMETRIC DETERMINATION OF NITRITE CONTENT IN CERTAIN COMMERCIAL DRIED MEAT PRODUCTS AND THEIR MICROBIOLOGICAL EFFECTS

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Production of nitrogenous compounds, nitrates and nitrites, rapidly increases, since these salts are frequently applied as additives in food, especially dried meat products. Addition of these compounds to dried meat products ensures their microbial protection, but also affects their consistency, color and taste. Previous studies have shown that dried meat products participate with 5 – 8 % of the daily intake of nitrate salts in the human body and that the intake from fruits and vegetables is the most common. However, investigation of the influence of nitrate salts from fruits and vegetables on human health show that this kind of intake has a dominant protective effect, particularly in coronary disease and ischemia. The toxicity of nitrate salts is connected with the formation of N-nitro compounds in the presence of proteins.

In this paper, the content of nitrites as additives in dried meat products was analyzed with the spectrophotometric method, followed by the comparison of the obtained results with the concentrations specified by the BIH laws. Dried meat products were selected from the group of pate, cold cuts, sausages and frankfurters. The efficiency of nitrate salts as additives was studied from the microbiological point of view. Also the interviews carried out among the student population at the University of Tuzla, give approximate insight into the amount of consumption of the examined products.

The results showed that all products on the market were within the limits permitted by the existing legislation, and that the estimated intake of these products in the student population should not significantly change the amount of daily intake of nitrites.

Key words: nitrites, dried meat products, legislation, spectrophotometric method.

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INVESTIGATION OF SOME INTERACTIONS BETWEEN Ca(II) AND Mg(II) IONS AND NONIONIC SURFACTANTS IN WATER USING TENSIOMETRIC METHOD

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Nonionic surfactants have an increasingly significant share in industrial production since they are used daily in different products, such as: washing and cleaning agents, food additives, flocculation agents, also in pharmaceutical industry, soil remediation, etc. Their ability to build complex species with Ca(II) and Mg(II) ions from water provides more efficient utilization of anionic surfactants contained in cleaning and washing agents. Reducing the concentration of anionic surfactants with achieving their high efficiency (due to increased resistance to the precipitation processes in hard water) also has a positive effect on their concentration in waste waters. For investigation of surfactant properties, such as: decreasing of surface tension, electrolytical conductivity, solubilization and emulsifying properties as well as their interactions with coexisting ions and compounds, conductometry, tensiometry and spectrometry are the most efficient methods. In this paper, effects of different structures of nonionic surfactants on their interactions with Ca(II) and Mg(II) ions were investigated using tensiometric method. Model systems containing cation-surfactant mixtures prepared with both: double distilled water and water for households in Tuzla Canton (with different hardness and coexisting ions concentration), were used. In preparation of model systems, nonionic surfactants with polyoxyethylene chains and straight structure (C₁₂E₉ and C₁₈E₂₀) and also with branched structure (C₁₄E₁₀ and C₁₄E_{4.5}) were selected. The results showed that decreasing of surface tension in investigated systems depends on both: the concentration of cations and the concentration of surfactants. It was found that in the area below the critical micellar concentration (CMC), increasing of Ca(II) and Mg(II) ions concentration induce decreasing of surface tension, as well as the change of surfactant structure. Above the CMC, this influence is negligible. It is assumed that the complex species formed in interactions between cations and surfactants are responsible for efficiency of nonionic surfactants in water solutions.

Key words: nonionic surfactants, Ca(II), Mg(II), tensiometric method.

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FTIR AND NIR STUDY OF HYDROGEN BONDS OF N-SUBSTITUTED CAPROAMIDES WITH TETRAHYDROFURAN AND DIETHYLEETHER

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Hydrogen bonding has a great importance in chemistry and biology. Secondary amides are particularly interesting since the hydrogen bonding of amide group is an important factor in determining the structure of proteins and polypeptides. This paper reports the results of FT-IR and NIR study of three caproamides (N-p-fluorophenyl caproamide, N-p-chlorophenyl caproamide and N-p-bromophenyl caproamide) in carbon tetrachloride solution and in presence of diethylether and tetrahydrofuran. The spectroscopic characteristics of the N-H...O hydrogen bonded complexes are given. Also, the equilibrium constants for 1:1 complex formation at 25°C were determined using Mid-IR and NIR measurements. Analyzed complexes were compared to complexes of some other secondary amides with same ethers [1-3] using Wards method cluster analysis.

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QUALITATIVE AND QUANTITATIVE DETERMINATION OF GLUCOSINOLATES FROM *LUNARIA ANNUA* (L.)

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Glucosinolates (thioglucosides) are multi-functional secondary plant metabolites which have long been of toxicological and pharmacological interest. Here, we report qualitative and quantitative investigation of glucosinolates in the wild-growing Brassicaceae plant, *Lunaria annua* (L.). Different plant parts (seed, root, stem, leaf, flower) were investigated to uncover individual glucosinolates throughout their breakdown products obtained by enzyme hydrolysis. The hydrolysis products were isolated by CH₂Cl₂ extraction and analysed by GC/MS. The major glucosinolates include **aliphatic** isopropylglucosinolate (*glucoputranjivin*), pent-4-enylglucosinolate (*glucobrassicinapin*), hex-5-enylglucosinolate and **with sulfur-containing side chains** 5-(methylsulfinyl)-pentylglucosinolate (*glucoalyssin*) and 6-(methylsulfinyl)hexylglucosinolate (*glucohesperin*). Other minor glucosinolates were also identified such as *sec*-butylglucosinolate (*glucocochlearin*), hept-6-enylglucosinolate, 4-(methylsulfonyl)butylglucosinolate (*glucoerucin*), 5-(methylsulfonyl)-pentylglucosinolate (*glucoberteroin*). Quantification of total glucosinolates was based on their alkaline degradation and subsequent reaction of released 1-thioglucose with ferricyanide. The reaction was followed spectrophotometrically using sinigrin as model glucosinolate. Total glucosinolate determined in *L. annua* seeds was 27.33 μmol/g dry weights.

**ODREĐIVANJE DIJASTAZE U MEDU: DIREKTNA
POTENCIOMETRIJSKA VS. SCHADE I PHADEBAS
METODA
HONEY DIASTASE DETERMINATION: DIRECT
POTENTIOMETRY VS. SCHADE AND PHADEBAS
PROCEDURES**

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Recently, we proposed [1] a new rapid method for the determination of honey diastase activity using direct potentiometric principles. The method is based on direct potentiometric determination of diastase after hydrolysis of starch from starch-triiodide complex. Standard Schade [2] procedure is time consuming and Phadebas [3] method is expensive comparing price/sample analyzed. They use DN unit for presenting the diastase activity. New method is cheaper and faster, and new unit for diastase activity, S, has been proposed. These three procedures have been compared, and results showed good mutual correlation.

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**VOLUMETRIJSKA SVOJSTVA VODENIH OTOPINA
FERULINSKE KISELINE PRI RAZNIM
TEMPERATURAMA
STUDIES ON VOLUMETRIC PROPERTIES OF FERULIC
ACID IN WATER AT VARIOUS TEMPERATURES**

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Ferulic acid (FA) (4-hydroxy-3-methoxycinnamic acid) is a ubiquitous phenolic compound in plant tissues, therefore, it constitutes a bioactive ingredient of many foods. FA is an abundant dietary antioxidant which may offer beneficial effects against cancer, cardiovascular disease, diabetes and Alzheimer's disease [1]. In this work, we were determined apparent molar volume (V_ϕ) of FA in water at different temperatures (T) and acid molality (m) from the density data (d) obtained with the help of a vibrating-tube Anton Paar DMA-4500 M densimeter. The limiting partial molar volumes ($\bar{V}$), the partial molar expansivity (E°), the isobaric coefficient of thermal expansion (α_p), and the interaction coefficient (S_V) of FA in water have also been computed. They were qualitatively correlated with the changes in the structure of water when FA is dissolved in it [2-4].

[1] Z. Zhao, M. H. Moghadasian, *Food Chem.* **109** (2008) 691.

[2] F. J. Millero, *Chem. Rev.*, **71** (1971) 147.

[3] L. G. Hepler, *Can. J. Chem.*, **47** (1969) 4613.

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FOTOKEMIJSKE TRANSFORMACIJE TIOFENSKIH ANALOGA *o*-DISTIRILBENZENA PHOTOCHEMICAL TRANSFORMATIONS OF THIOPHENE *o*-DISTYRYLBENZENE ANALOGUES

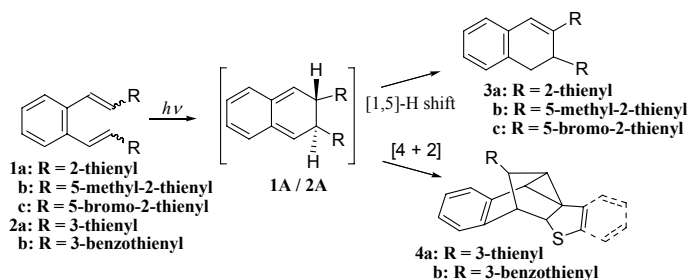
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From the mechanistic and preparative point of view the stilbenes are the most studied chromophores. Their synthesis is relative simple and they possess interesting photophysical and photochemical properties. Distyrylbenzenes [1] and their heteroaromatic analogues are particularly interesting. Due to their expanded π -electron delocalization versatile photoproperties could be induced, important in the chemistry of materials, especially optoelectronics [2].



To investigate the photochemical reactions of heterocyclic analogues of stilbene compounds styryl-thiophenes were studied. Different substituted β,β' -dithiophene derivatives of *o*-distyrylbenzenes with sulphur at position 2 (**1a-c**) and position 3 (**2a-b**) were prepared. The photochemistry of 2-substituted β,β' -dithiophene derivatives of *o*-distyrylbenzenes **1a-c** showed that along with the isomerization of double bonds the main photochemical process was 6π -electrocyclization and formation of dihydronaphthalene derivatives **3a-c**, respectively. Irradiation of 3-substituted dithiophene derivatives **2a** and **2b** provided the fused tricyclic compounds **4a** and **4b**, respectively, *via* the same dihydronaphthalene intermediate by [4+2]-cycloaddition with thiophene.

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[2] J. L. Segura and N. Martin, *J. Mater. Chem.* **10** (2000) 2043-2435.

**KARKTERIZACIJA ASFALTENA IZ NAFTI
RAZLIČITOG PODRIJETLA
CHARACTERIZATION OF ASPHALTENES FROM
CRUDES OF DIFFERENT ORIGIN**

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Jedan od većih problema koji se javlja prilikom rafinerijske prerade naftnih mješavina, a posebice mješavina koji u svojem sastavu sadrže vrlo teške nafte je njihova nekompatibilnost. Nakon određenog vremenskog razdoblja tijekom njihovog skladištenja i rafinerijske prerade dovodi do flokulacije i taloženja asfaltena. Nekompatibilnost naftnih mješavina može uzrokovati cijeli niz nepoželjnih i ozbiljnih oštećenja većeg broja procesnih jedinica i to: spremnika sirove nafte, izmjenjivača topline, destilacijskih kolona (atmosferske i vakuum) te peći za predzagrijavanje nafte. Prema tome za razumijevanje mehanizma procesa flokulacije i taloženja asfaltena u pojedinim naftnim mješavina te kao prevencija njihovog nastanka provedena je njihova karakterizacija. U ovom radu provedena je karakterizacija asfaltena dobivenih iz nafti različitog podrijetla nakon njihovog taloženja u n-heptanu mikroskopskim pregledom, spektroskopskim tehnikama i elementarnom analizom. Istraživanja su pokazala da sastav istaloženih asfaltena u naftama različitog podrijetla u različitim otapalima vidljivo se razlikuju po morfološkoj strukturi i sastavu. Također je utvrđeno je da vrsta otapala ima vrlo važan utjecaj na sastav i strukturu istaloženih asfaltena.

FOTOKEMIJA NOVIH BUTADIENSKIH DERIVATA: UTJECAJ SUPSTITUENTA NA FOTOINDUCIRANA SVOJSTVA

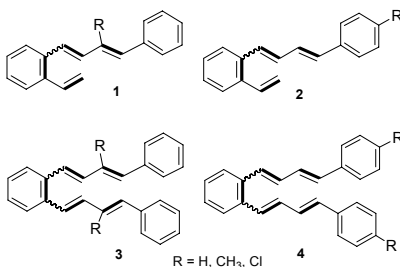
PHOTOCHEMISTRY OF NEW BUTADIENE DERIVATIVES: INFLUENCE OF THE SUBSTITUENT ON THE PHOTOINDUCED BEHAVIOR

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In order to prepare novel polycyclic structures by photochemical methodology, new substituted butadiene derivatives **1-4** were synthesized and the photochemistry of these prolonged conjugated systems was studied. Our previous results [1,2] on the photochemistry of the unsubstituted (R = H) and substituted butadienes **1** and **3** (R = CH₃) showed interesting diverse photochemistry and photophysics of these compounds of rather similar structures.



The introduction of chloro-substituent(s) in the unsubstituted compounds **1-4** changes the course of the photoreaction in several instances due to dramatic steric and electronic effects of these substituents on the photochemical features of the molecule. Understanding of the governing effects of the substituents on the photochemical reactions of these new butadiene derivatives and elucidation of the reaction mechanisms of the photoproducts formation, make the synthesis of these systems suitable for directing the photoreaction to different interesting structures which can be further transformed and functionalized.

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IMPEDIMETRIJSKI Au-NTA SENZOR ZA ODREĐIVANJE OLOVA IMPEDIMETRIC Au-NTA SENSOR FOR LEAD DETERMINATION

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Recently, we have developed a chemically modified gold electrode by using nitrilotriacetic (NTA) functionalized thiol monolayers prepared by soaking a cysteamine attached gold electrode in an aqueous solution of NTA. Thiol monolayers prepared on gold electrodes serve as the anchor layers to immobilize NTA molecules using EDC/NHS chemistry.

Existence of each layer on the top of disc gold electrode was confirmed by cyclic voltammetry and electrochemical impedance spectroscopy (EIS) in acidic and basic solutions using $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox pair.

The electrode prepared in this way was used for lead determination. The binding of Pb^{2+} onto the modified electrode was successfully performed in a wide range of tested concentrations and was confirmed by EIS. Electrode response ($\log \Delta R_{\text{ct}}$) was linearly proportional to $\log c(\text{Pb}^{2+})$ with squared correlation coefficient $R^2 = 0.9865$ for measurements in acetic buffer pH = 4.6 and $R^2 = 0.9931$ for measurements in boric buffer pH = 7.0 at micromolar concentration level.

**ODREĐIVANJE GLUKOZE U HRVATSKIM VINIMA
AMPEROMETRIJSKIM BIOSENZOROM I
SPEKTROFOTOMETRIJSKI
DETERMINATION OF GLUCOSE IN CROATIAN WINES
BY AMPEROMETRIC BIOSENSOR AND
SPECTROPHOTOMETRICALLY**

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So far we developed amperometric biosensors for glucose determination based on glucose oxidase (GOx) enzyme in many different ways and applied them for various analytes in food analysis [1,2]. In this work GOx was immobilized on the surface of modified graphite electrode by entrapment into palladium hexacyanoferrate (PdHCF) hydrogel and the biosensor prepared in this way was used for determination of glucose in Croatian wines using standard addition method. The electrochemistry of enzyme-modified electrode was investigated by cyclic voltammetry and amperometry under batch conditions. The response of biosensor was tested as a function of selected organic solvents (methanol, ethanol, acetone and acetonitrile) containing phosphate buffer solution (pH = 5.5) at -50 mV against a reference $\text{Hg} | \text{Hg}_2\text{Cl}_2 | 3 \text{ M KCl}$ electrode. The same samples were, for comparison, analysed with the spectrophotometric method as well, based on two stage enzymatic reactions which results, after oxidation of glucose, in formation of a coloured potassium hexacyanoferrate(III) in solution. The results have shown that NiHCF as redox mediator offer better electrocatalytic efficiency for hydrogen peroxide reduction compared with bare graphite electrode. Addition of organic solvents ($\varphi = 10\text{--}60 \%$) decreased the biosensor response, therefore the determination of glucose in Croatian wines has been performed in phosphate buffer (pH = 5.5). The linear range was obtained in the concentration range from 0.1 to 0.6 mM with a squared correlation coefficient of 0.9994. Correlation between the results obtained by the GOx biosensor and spectrophotometrically was acceptable although the biosensor determination is much more rapid. The proposed amperometric GOx biosensor has been successfully applied for determination of glucose in some red and white Croatian wines. Its analytical performance in terms of high activity, long life and reasonable accurate glucose determination can be recommended in food industry for quality control of wines as well as during fermentation process, when glucose is transformed into alcohol.

[1] A. Ninčević Grassino, S. Milardović, Z. Grabarić and B. S. Grabarić, *Food Chem.* **125** (2011) 1335.

[2] A. Ninčević Grassino, S. Milardović, Z. Grabarić and B. S. Grabarić, *Food Res. Int.* **47** (2012) 368.

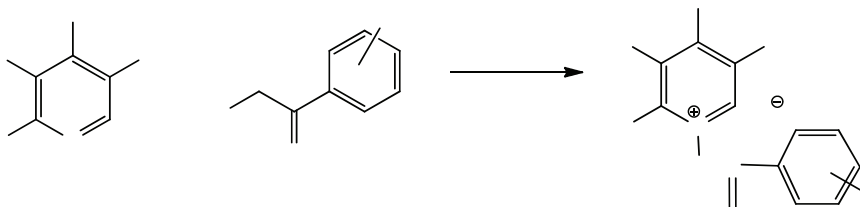
KVATERNIZACIJA PIRIDOKSAL-OKSIMA SA FENACIL-BROMIDIMA POD UTJECAJEM MIKROVALNOG ZRAČENJA MICROWAVE-ASSISTED QUATERNIZATION OF PYRIDOXAL-OXIME WITH PHENACYL BROMIDES

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U radu su izvedene reakcije kvaternizacije piridoksal-oksima sa supstituiranim fenacil-bromidima ($R = H, C_6H_5, Cl, Br, F, CH_3, OCH_3, NO_2$) pomoću novih, ekološki prihvatljivijih metoda. Budući da zaštita okoliša postavlja danas velik izazov i obvezu za kemičare istražen je zanimljiv pristup "zelenoj" kemiji tj. nove kemijske metode sinteze koje su manje štetne po okoliš. Ispitane su reakcije kvaternizacije aktivirane mikrovalnim zračenjem u prisustvu i bez prisustva otapala. Razvijene su nove jednostavne metode sinteze kvaternih piridinijevih soli u kućnoj mikrovalnoj pećnici [1]. U usporedbi s klasičnom reakcijom kvaternizacije [2] pokazano je da su reakcije pod utjecajem mikrovalnog zračenja odnosno nekonvencionalne zelene metode pripreme kvaternih piridinijevih soli, učinkovitije i brže te da produkt nastaje u većem prinosu.



[1] K. R. Seddon, M. Deetlefs, *Green Chem* **5** (2003) 181.

[2] D. Gašo-Sokač, M. Katalinć, Z. Kovarik, V. Bušić, S. Kovač, *Chemico-Biological Interactions* **187** (2010) 234–237.

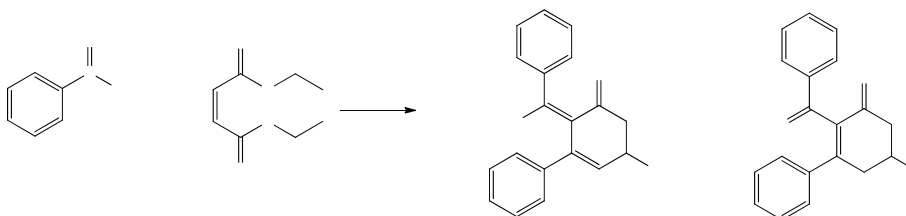
MICHAEL-OVA KONDENZACIJA POD UTJECAJEM MIKROVALNOG ZRAČENJA MICHAEL CONDENSATION PROMOTED BY MICROWAVE IRRADIATION

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Aktivacija mikrovalnim zračenjem kao nekonvencionalnim energetske izvorom postala je veoma popularna i korisna metoda organske kemije. Danas se mikrovalno ili dielektrično zagrijavanje primjenjuje kao alternativa klasičnom zagrijavanju, a temelji se na apsorpciji elektromagnetskog zračenja koje se pretvara u toplinu, što otvara velike mogućnosti primjene u kemiji i kemijskom inženjerstvu. Osnovne prednosti sinteze pod utjecajem mikrovalova u odnosu na klasičnu sintezu su znatno skraćanje reakcijskog vremena (s nekoliko sati ili dana na nekoliko minuta), bolje iskorištenje i smanjenje udjela nusprodukata [1]. Cikličke oksokiseline istražuju se zbog svoje biološke aktivnosti budući da djeluju kao spolni hormoni [2].



U ovom je radu izvedena reakcija Michael-ove kondenzacije acetofenona i dietil-maleata pod utjecajem mikrovalnog zračenja uz katalitičku količinu natrijeva etoksida [3]. Identificirani su tautomerni produkti 4-[hidroksi(fenil)metilen]-3- fenil-5-oksocikloheks-2-en karboksilna kiselina (1) i 4-benzoil-3-fenil-5-oksocikloheks-3-en karboksilna kiselina (2). U usporedbi s istom reakcijom kondenzacije bez utjecaja mikrovalnoga zračenja enolni je produkt dobiven u znatno većem prinosu i kraćem reakcijskom vremenu.

[1] I. Zrinski, M. Eckert-Maksić, *Kem. Ind.* 54 11(2005) 469-476.

[2] Z. Lazarević, J. Vorkapić-Furač, J. Mühl, *Monatsh. Chem.* **123** (1992) 1175-1179.

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SEPARACIJA I KVANTIFIKACIJA AMINOKISELINA PRIMJENOM ELEKTROFOREZE NA MIKROČIPU AMINO ACID SEPARATION AND QUANTIFICATION USING MICROCHIP ELECTROPHORESIS

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Microchip electrophoresis (MCE) is a mode of capillary electrophoresis (CE) in which analysis is performed in a miniaturized device containing microchannels. The concept of MCE was first introduced by Harrison et al. [1] and is widely applied for small biological molecule separations, numerous inorganic cations and anions etc. The quantity of sample actually injected into the microchannel of a chip device is typically in the picoliter (pL) range compared to nanoliter (nL) in CE and microliter (μ L) range in liquid chromatography. In the investigated presented, several amino acids of different chemical nature were investigated and successfully separated as a single species and in a mixtures of various compositions. A capacitively coupled contactless conductivity detector (C^4D) operating at several hundreds kHz was used for their detection. The influence of the following parameters on the separation ability was investigated: injection voltage, injection time, separation voltage, separation time. The background electrolyte and buffer composition were thoroughly studied in order to optimize the separation. The used disposable chip is fabricated out of poly(methyl methacrylate) (PMMA). The linear response region for each particular amino acid investigated, both single and in a mixture, was determined using linear regression. Detection limits for all the amino acids investigated were below 1 mg/mL.

[1] D.J. Harrison, A. Manz, Z. Fan, H. Luedi, H.M. Widmer, *Anal. Chem.* **64** (1992) 1926.

PRIMJENA MIKROEKSTRAKCIJE VRŠNIH PARA NA KRUTOJ FAZI ZA KARAKTERIZACIJU AROME AUTOHTONOG SIRA IZ "MJEŠINE"

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Autohtoni sir iz "Mješine" nakon sirenja se sprema u obrađeni miješ od ovčje ili kozje kože. Sir iz "Mješine" prave u mnogim planinskim krajevima Dalmacije, a gotovo posvuda ga izrađuju na sličan način. Nakon sirenja, mješina se puni sirom koji se prethodno ne mrvči, već se reže na kriške. Kriške se zatim slažu sloj po sloj, a svaki sloj se dobro posoli. Ako je sir dobro zbijen, a mješina dobro zatvorena, sir može stajati veoma dugo [1]. U ovom radu analiziran je kemijski profil isparljivih spojeva uzoraka sira iz mješine dobiven mikroekstrakcijom vršnih para na krutoj fazi (HS-SPME) koristeći vlakna s PDMS/DVB i DVB/CAR/PDMS prevlakama. Analiza izoliranih isparljivih spojeva provedena je vezanim sustavom plinska kromatografija-spektrometrija masa (GC-MS) koristeći kolonu HP-5MS. Najzastupljeniji spojevi su bili: 3-metil-but-1-ol, etil-acetat, butanska kiselina, izoamil-acetat, etil-heksanoat, etil-kaprilat i octena kiselina. Jako reducirajući uvjeti u siru favoriziraju nastanak alkohola iz aldehida i ketona preko reakcija koji uključuje i alkohol dehidrogenazu. Prisutnost primarnog alkohola kao što je 3-metilbutan-1-ol, koji je nađen i u drugim vrstama sira, indicira redukciju aldehida koji nastaju iz leucina [2]. Isparljivi spojevi prisutni u uzorcima sira uglavnom potječu iz procesa lipolize i katabolizma aminokiselina.

[1] Nikola Zdanovski, Ovčje mljekarstvo-proizvodnja i prerada ovčjeg mljeka, Poljoprivredni nakladni zavod, Zagreb 1947, 96.

[2] Francisco José Delgado, José Gonzáles-Crespo, Ramón Cava, Rosario Ramírez, *Food Chem.*, **129** (2011) 1156.

KEMIJSKO I BIOKEMIJSKO INŽENJERSTVO
CHEMICAL AND BIOCHEMICAL ENGINEERING

**MOLEKULARNO MODELIRANJE KAO METODA
ISPITIVANJA INTERAKCIJE MELATONINA S
LAKTOPEROKSIDAZOM**
**MOLECULAR MODELING AS A METHOD OF TESTING
MELATONIN – LACTOPEROXIDASE INTERACTION**

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Melatonin je glavni sekretorni produkt pinealne žlijezde, a enzimatski se sintetizira iz serotonina. Podaci dobiveni do sada pokazuju da melatonin izravno predstavlja čistač slobodnih radikala, dok neizravno ima antioksidacijsko djelovanje. Osnovna osobina laktoperoksidaze u laktoperoksidaznom sistemu je da katalizira oksidaciju tiocijanata i halogenida, u prisustvu hidrogen peroksida, stvarajući hipotiocijanatnu kiselinu koja pokazuje antimikrobna svojstva na veliki broj mikroorganizama. Laktoperoksidaza se intenzivno istražuje već niz godina, a prisutna je, osim u mlijeku, u mnogim tekućinama različitih dijelova tijela. U radu je istražena interakcija, kao i mogući način vezivanja melatonina na aktivno mjesto enzima, željezo-protoporfirin IX, primjenom SPARTAN '08 programa za molekularno modeliranje. Rezultati, s obzirom na dobivene dužine veze, geometriju i izračunate vibracijske frekvencije, IR spektre, ukazuju na nemogućnost vezivanja melatonina na tzv. aktivno mjesto laktoperoksidaze. Simuliranjem moguće dužine veze između porfirinskog željeza i melatonina, pokazano je da melatonin stvara slabu vezu sa željezom, koja nije ostvariva usljed djelovanja proteinskog matriksa i konformacije laktoperoksidaznog aktivnog mjesta.

Ključne riječi: laktoperoksidaza, LP sistem, aktivno mjesto, melatonin, SPARTAN

**ANALIZA FIZIKALNIH SVOJSTAVA POROZNOG
AMONIJEVOG NITRATA
ANALYSIS OF PHYSICAL PROPERTIES OF POROUS
AMMONIUM NITRATE**

Goran Raosavljević, Ismaiel Warde

PETROKEMIJA d.d., TVORNICA GNOJIVA, Aleja Vukovar 4, KUTINA

At the plant AN/KAN2, located within PC Fertilizer production that is part of fertilizers factory Petrokemija d.d., the main product along with calcium ammonium nitrate (KAN) is porous ammonium nitrate, which is used for producing explosives. Depending on the amount of oil that can be absorbed, we differ porous ammonium nitrate with 6% and 12% absorption. The final product must have all the physical properties within the defined limits, which is not always an easy task. Physical properties of the final product depend on both process parameters and external conditions.

The purpose of this study was to show the dependence of physical properties of ammonium nitrate: static strength, curing, bulk density, granulometric composition and absorption on process and external conditions that changes during the year. In order to maximize the credibility of the results, the results of all analysis obtained in period from year 2000. to 2011. in accredited laboratory – CC Quality control were taken into consideration. The results are tabulated and presented graphically. Based on our experience and obtained results it can be concluded that the physical properties of AN are more stable during the winter, when the static strength is higher and curing is tending to zero, while in summer period they vary. Since ammonium nitrate is very hygroscopic, the assumption is that its physical properties are affected by changes in air humidity.

**ISPITIVANJE UTJECAJA LITIJEVOG
MONTMORILONITA NA STRUKTURU I TOPLINSKA
SVOJSTVA POLI(ETILEN-OKSIDA)
AN INVESTIGATION OF THE EFFECT OF LITHIUM
MONTMORILLONITE ON THE STRUCTURE AND
THERMAL PROPERTIES OF POLY(ETHYLENE OXIDE)**

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The technological importance of solid electrolytes, for which poly(ethylene oxide) (PEO) is often used, is continuously increasing. The main drawback of PEO as a solid electrolyte is its poor ionic conductivity at room temperature due to high crystallinity, since the ionic conductivity mainly takes place in the amorphous phase. Incorporation of inorganic nanophases such as nanoclays in the PEO matrix is one of the ways to decrease its crystallinity and enhance ionic conductivity. In this work, the effect of lithium montmorillonite (LiMMT) as nanofiller on the crystallinity, glass transition temperature, melting temperature and thermal stability of PEO is investigated. PEO/LiMMT samples (100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90 i 0/100 by weight) were prepared by melt intercalation method. Differential scanning calorimetry shows that both the melting point and glass transition temperature of PEO are lowered as the amount of LiMMT increases. The crystallinity of PEO decreases with increasing amount of LiMMT and completely disappears between 70 and 80 mass % of LiMMT, which is confirmed by infrared spectroscopy.. Thermogravimetric analysis indicates that the degradation of PEO and PEO/LiMMT samples occurs through one degradation step and that LiMMT lowers the thermal stability of PEO up to 50°C.

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REMOVAL OF COPPER IONS IN WASTEWATER BY GEOPOLYMERS SYNTHESIZED FROM FLY ASH

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The removal efficiency of copper ions in aqueous solutions was investigated by adsorption process on pure and modified geopolymer, synthesized from fly ash. A type F (as defined in ASTM C618) fly ash from the Croatian power plant Plomin 2 (Plomin) was used in the present study.

The batch experiments were carried out as a function of solute concentration at constant temperature (23 °C) and particle size (90-500 nm). The sorption capacity of copper ions increases with the initial concentrations of solute and for the modified geopolymer it reaches its maximum value at $q_e = 0.712 \text{ mmol g}^{-1}$ and for the pure geopolymer it reaches its maximum value at $q_e = 0.814 \text{ mmol g}^{-1}$. Kinetic studies based on Lagergren pseudo-first order, Ho pseudo-second order, Ritchie second-order and Elovich rate equations were used to test experimental rate data. All the models were analyzed using nonlinear regression technique.

The results obtained indicate that, both pure geopolymer and modified geopolymer could be used as alternative materials for the wastewater treatment. Nevertheless, pure geopolymer shows a slightly better efficiency. Kinetic study has shown that the best fit is achieved when the Elovich model was applied.

NANOSENZORI ZA DETEKCIJU PLINOVA OTOPLJENIH U TRANSFORMATORSKOM ULJU NANOSENSORS FOR DETECTION OF GASES DISSOLVED IN TRANSFORMER OIL

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Transformatorsko ulje i papir organski su materijali od kojih se sastoji izolacijski sustav uljnih transformatora. Tijekom rada transformatora, uslijed starenja izolacije, električnih i termičkih naprežanja, razvijaju se karakteristični plinovi (vodik, metan, etan, etilen, aceten, ugljikov monoksid i ugljikov dioksid) topivi u ulju. Nastajanje plinova intenzivnije je uslijed kvara ili greške, a pojedini plinovi i njihovi omjeri specifični su za pojedine greške (parcijalna izbijanja, pregrijavanje, električni luk kroz ulje itd.). Metoda za određivanje plinova otopljenih u transformatorskom ulju je normizirana. Ispitivanje se provodi ekstrakcijom plinova iz ulja i kromatografskom analizom uzorka plina. U praksi se koristi već dugi niz godina i dokazala se kao jedna od najučinkovitijih metoda za otkrivanje kvarova u transformatoru. Kontinuirana analiza plinova otopljenih u ulju omogućava rano otkrivanje kvara transformatora. U tu svrhu koriste se on-line monitoring sustavi. Komercijalno su dostupni sustavi koji koriste različite metode: detekcija termičke vodljivosti, plamena ionizacija, infracrvena spektroskopija, fotoakustična spektroskopija, itd. Razvojem nanotehnologije dolazi do njene primjene u području senzorike. Nanosenzori za detekciju plinova otopljenih u transformatorskom ulju još su u fazi istraživanja. Prednost nanosenzora u odnosu na do sada dostupne on-line metode je mogućnost analiziranja plinova u ulju bez ekstrakcije, dobra osjetljivost i brz odziv. U radu je dan pregled nanosenzora za detekciju plinova u transformatorskom ulju te procjena mogućnosti njihove primjene u komercijalne svrhe.

**PRIMJENA SOFTVERSKIH SENZORA ZA PROCJENU
SADRŽAJA BENZENA U REFORMATU
SOFT SENSORS APPLICATION FOR THE ESTIMATION
OF BENZENE CONTENT IN REFORMATE**

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As vehicle emission standards become more stringent there is an increasing need for continuous monitoring of benzene content in gasoline. Since the on-line analyzers are often unavailable, and laboratory analyses are infrequently, soft sensors for benzene content estimation of reformat are developed. Experimental data is acquired from the refinery distributed control system (DCS) and include continuously measured variables and analyzer assays. Dynamic models based on Finite Impulse Response (FIR) and Output Error (OE) identification methods are presented. To avoid a trial and error procedure, genetic algorithm model order optimizing is proposed. The models are implemented on advanced application module within DCS where the benzene content is calculated based on dynamic polynomial models and stored in process history database. The results show very good matching with experimental data on validation set, thus proving their usefulness for on-line estimation of benzene content in reformat. Moreover, since the process analyzer for benzene content is often out of order due to maintenance the model replaces on-line analyzer. Performance is validated comparing the results with laboratory analyzes carried out 2 or 3 times a day.

ISPITIVANJE UTJECAJA PROCESNIH PARAMETARA NA IZOMERIZACIJU *n*-HEKSANA U SMJESI S LAKIM BENZINOM THE INFLUENCE OF PROCESS PARAMETERS ON THE ISOMERIZATION OF *n*-HEXANE IN THE MIXTURE WITH LIGHT NAPHTHA

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Izomerizacija je sekundarni rafinerijski proces kojim se dobiva tzv. *izomerizat* – *benzin*, jedna od sastavnica motornog benzina. Tijekom procesa dolazi do pretvorbe *n*-alkana u izoalkane čime se postiže povećanje oktanskog broja, tj. povećanje kvalitete benzina. Uslijed sve strožih zakonskih propisa u pogledu kvalitete goriva i zaštite okoliša proces izomerizacije dobiva sve više na važnosti jer omogućuje proizvodnju kvalitetnog produkta na ekološki prihvatljiv način, bez sadržaja sumpora i aromata. U ovom radu ispitivani su utjecaji temperature, prostorne brzine (*LHSV*), omjera vodik/ugljikovodici (H_2/HC) i udjela *n*-heksana u sirovini na izomerizaciju realne sirovine iz Rafinerije nafte Rijeka, INA d.d. (laki benzin) primjenom $Pt/SO_4^{2-} - ZrO_2$, tzv. cirkonij sulfat katalizatora. To je čvrsti difunkcionalni katalizator (sadrži kisele i metalne katalitički aktivne centre) koji ne zahtijeva primjenu dodatnih kapljevitih promotora kiselosti što sam proces izomerizacije čini također ekološki prihvatljivim. Eksperimenti su provedeni dvjema metodama: metodom *One Factor At a Time* (OFAT) i metodom *Design of Experiments* (DOE). Ispitivanjima provedenim pomoću OFAT metode utvrđeno je da konverzija *n*-heksana u njegove izomerne spojeve raste porastom temperature u istraživanom području od 130 °C do 170 °C. Zatim je utvrđeno da se najveće konverzije *n*-heksana ostvaruju na najmanjim vrijednostima *LHSV* od 1 h⁻¹, dok konverzija *n*-heksana u ovisnosti o omjeru H_2/HC pokazuje maksimum koji se povećanjem temperature pomiče prema većim vrijednostima omjera H_2/HC . Ispitivanja prema DOE metodi provedena su primjenom Box-Behnkenovog plana pri čemu je proces opisan razvijenim empirijskim modelom. Validacija modela provedena je statističkom metodom analize varijance. Rezultatima DOE eksperimenata i modeliranja potvrđene su ovisnosti utvrđene na temelju rezultata OFAT eksperimenata.

**MODELIRANJE I OPTIMIZACIJA PROCESA
DESTILACIJE PRI PROIZVODNJI AKTIVNIH
FARMACEUTSKIH SASTOJAKA
PROCESS MODELING AND OPTIMIZATION OF
DISTILLATION IN MANUFACTURE OF ACTIVE
PHARMACEUTICAL INGREDIENTS**

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Tijekom razvoja procesa proizvodnje aktivnih farmaceutskih supstancija (API) često se koriste separacijski procesi destilacije otapala. Briga za okoliš definira korištenje manjih količina otapala tijekom proizvodnje. Stoga se optimiranje provodi na način da se minimizira vrijeme destilacije i količina otapala. Tijekom zamjene otapala (polazno otapalo s drugim otapalom) proces se definira kroz procesne specifikacije. Stoga uporaba procesnih simulatora (*DynoChem*) i modeliranje procesa destilacije kroz inženjerska načela omogućuju bolje razumijevanje procesa destilacije i ispunjavanje zahtjeva procesa. Simulacija omogućava predviđanje vremena destilacije i profila sastava tijekom operacije zamjene otapala. Moguća su dva načina rada destilacije: (1) održavanje konstantnog volumena dodavanjem drugog otapala, i (2) "šaržiraj i otpari", gdje se sadržaj reaktora destilira do minimalnog volumena, a zatim se drugo otapalo dodaje do maksimalnog volumena. U oba slučaja destilacija prestaje kada ciljni sastav polaznog otapala bude postignut. Napravljena je simulacija procesa gdje se provodi zamjena smjese diklormetana i vode sa acetonom. Zahtjev procesa je da sadržaj diklormetana ne smije biti veći od 1 %, te da temperatura ne smije prijeći 40 °C. Ispitan je procesni prostor: brzina dodavanja acetona, minimalni volumen smjese, tlak u destilacijskoj koloni, te ukupna utrošena količina acetona tijekom zamjene. Simulacijom je utvrđena bilanca tvari i određeno da tri dodavanja acetona mogu ispuniti procesne zahtjeve, što je eksperimentalno potvrđeno. Određeno je optimalno područje parametara metodologijom određivanja procesnog prostora (eng. *Design Space*), te robusnost procesa obzirom na navedene parametre.

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KOROZIJSKO PONAŠANJE ŽELJEZA U FLUORIDNOM MEDIJU CORROSION BEHAVIOR OF IRON IN FLUORIDE MEDIA

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U radu su istraživani mehanizam i kinetika rasta, kao i svojstva oksidnog filma formiranog na željezu u fluoridnom mediju u ovisnosti o pH vrijednosti i sadržaju fluoridnih iona koji stvaraju korozivni okoliš u procesu proizvodnje aluminija. Istraživanje je provedeno primjenom cikličke voltametrije i elektrokemijske impedancijske spektroskopije u deaeriranim otopinama NaF koncentracija 0,01 i 0,1 mol L⁻¹ pri različitim pH vrijednostima (4,5, 5,5 i 6,5). Rast oksidnog filma na željezu, u potenciodinamičkim uvjetima, karakteriziran je pojavom "strujnog platoa" zabilježenog na cikličkim voltamogramima, a analiza dobivenih rezultata pokazala je kako se rast oksidnog filma odvija migracijom iona u električnom polju niske jakosti. Određene su kinetičke veličine rasta oksidnog filma, elektronska provodljivost oksida ($\sim 10^{-12}$ S cm⁻¹), kao i jakost električnog polja kroz oksid ($\sim 10^6$ V cm⁻¹). Debljine oksidnih filmova dobivene analizom anodne strujne krivulje pokazuju kako se tanji film boljih zaštitnih svojstava formira u otopini niže koncentracije i više pH vrijednosti (za 0,01 mol L⁻¹ NaF, pH 6,5 $d = 1,37$ nm). Vrlo visoka vrijednost od 41,46 nm za debljinu pasivnog filma u otopini NaF koncentracije 0,1 mol L⁻¹ pri pH 4,5 upućuje na jako hidratizirani, rahli sloj. Impedancijska mjerenja provedena su na potenciostatski formiranim oksidnim filmovima nakon stabilizacije elektrode (30 minuta) na potencijalu otvorenog kruga. Pri svim ispitivanim uvjetima zabilježeni su niski otpori filma koji ne prelaze 70 kΩ cm², a vrijednost otpora, jednako kao i OCP, opada s porastom koncentracije F⁻ i snižavanjem pH. U istom smjeru zabilježen je porast kapaciteta filma od 53 μF cm⁻² za otopinu koncentracije 0,01 mol L⁻¹ pH 6,5 do 570 μF cm⁻² za otopinu koncentracije 0,1 mol L⁻¹ pH 4,5. Rezultati provedenih istraživanja pokazuju kako brzina korozije željeza raste sa snižavanjem pH vrijednosti i povećanjem koncentracije fluoridnih iona. U otopini NaF koncentracije 0,01 mol L⁻¹ pri smanjenju pH od 6,5 do 4,5 brzina korozije povećala se gotovo dvostruko, od 0,25 μg cm⁻² h⁻¹ do 0,48 μg cm⁻² h⁻¹, a u otopini NaF koncentracije 0,1 mol L⁻¹ pri istoj promjeni pH povećanje iznosi gotovo dvadeset puta.

Ključne riječi: željezo, anodni film, fluoridi, ciklička voltametrij, elektrokemijska impedancijska spektroskopija

FERMENTACIJA NA ČVRSTOJ PODLOZI RAZLIČITIH LIGNOCELULOZNIH SUPSTRATA S

Phanerochaete chrysosporium

SOLID-STATE FERMENTATION OF DIFFERENT LIGNOCELLULOSE SUBSTRATES USING

Phanerochaete chrysosporium

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In recent years, there has been an increasing interest in degradation of lignocellulosic materials due to their use as substrates for biofuels and different bioproducts production. Apart from agro-food industry, wood industry is also a generator of large amounts of lignocellulosic residues. The aim of this study was to perform solid-state fermentation of *Phanerochaete chrysosporium* using different lignocellulosic materials. Solid-state fermentation of *P. chrysosporium* was carried out using sawdust from three wood species (beech, cerris and oak) as substrates in laboratory flasks at 27 °C for 45 days. The chemical composition of samples collected before and after fermentation was analyzed, e.g. dry matter content, ash, total extractives, cellulose, lignin and nitrogen contents were determined using standard methods. The obtained results indicate good degradation capacity of *P. chrysosporium* when cultivated on cerris and beech sawdust.

Keywords: lignocellulose, solid-state fermentation, *P. chrysosporium*

ODREĐIVANJE VOLUMNOG KOEFICIJENTA PRIJENOSA KISIKA U MIKROREAKTORU ESTIMATION OF VOLUMETRIC OXYGEN TRANSFER RATE IN A MICROREACTOR

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Mikroreaktori se definiraju kao reaktorski sustavi izvedeni u mikromjerilu. Čini ih mreža mikrokanala u rasponu promjera od 10 μm do 300 μm . Male dimenzije kanala osiguravaju čitav niz prednosti pri korištenju mikroreaktora kao što su veliki omjer međufazne površine i volumena reaktora, intenzivan prijenos tvari i energije, mali utrošak reaktanata i katalizatora, fleksibilnost u kapacitetu i dizajnu, mali investicijski i operativni troškovi, te lako uvećanje procesa. Zbog brojnih prednosti mikroreaktori imaju primjenu u širokom spektru reakcija, od provođenja reakcija s nestabilnim međuproduktima, preko sinteza u nekoliko stupnjeva do višefaznih reakcija. Kao predmet velikog broja istraživanja posebno su zanimljive višefazne reakcije u sustavima plin–kapljevina. U takovim sustavima prijenos tvari je proporcionalan međufaznoj površini, koja je kod konvencionalnih makrosustava relativno mala. Sustavi plin–kapljevina u biotehnologiji se posebno istražuju u kontekstu biotransformacija u kojima je jedan od supstrata kisik. Osiguravanje optimalne koncentracije otopljenog kisika u mikroreaktoru omogućava postizanje veće konverzije i veće produktivnosti u procesu. U svrhu optimiranja i unaprjeđenja reakcija koje se u mikroreaktorima provode u sustavima plin–kapljevina, a nakon definiranja optimalnih režima strujanja, potrebno je odrediti volumne koeficijente prijenosa tvari. Cilj ovog rada je odrediti volumni koeficijent prijenosa kisika u sustavu zrak–voda u mikroreaktoru. U svrhu određivanja volumnog koeficijenta prijenosa kisika korištena je reakcija biotransformacije glukoze u glukonsku kiselinu uz prisustvo enzima glukoza oksidaze. Eksperimenti su provedeni u mikroreaktoru volumena 6 μL s tri ulaza i dva izlaza. Na ovaj način procijenjen volumni koeficijent prijenosa kisika u mikroreaktoru može se koristiti pri optimiranju procesa biotransformacija kataliziranih enzimima ovisnim o kisiku.

SEPARATION OF RACEMIC MIXTURES BY MEMBRANE SEPARATION PROCESSES

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A racemic mixture contains equal amounts of left- and right-handed enantiomers. Due to chiral centers, enantiomers are able to rotate plane-polarized light in opposite directions. Despite enantiomers exhibit identical properties in the achiral environment, should be considered as different chemical compounds because they often differ tremendously in effectiveness, pharmacological activity and pharmacokinetic profile, since the modules with which they interact in biological systems are also optically active [1]. As the model substance was chosen racemic mixture of α -pinene, the two enantiomers (R), (S)- α -pinene respectively due to it's suitable size and structure. α -pinene is used as a gentle diuretic, for rheumatism palliation and for bellows de-tension. In aromatherapy like respiratory stimulant during treating colds or pneumopathy. During pervaporation experiments the membrane was fixed in the cell and immersed in the liquid feed. The pervaporate is carried away by vacuum (or sweeping gas) and captured in the reservoir. During pertraction experiments the membrane was placed between the feed and receiving phase of the pertraction cell. Analysis was done by GCMS-Shimadzu QP2010, chiral column β -dex 0.25 μ m(Restek), T program: 60 °C/1min, rate 2.5°C/min -> 80 °C / 5 min, split 100, He column flow rate 0.7 ml/min. We choose three types of membranes with immobilizing chiral selector (AN-VImEt+L-Lactate40, SNCB6KIL5% and AN-VBCI-TPh(+)+L-Lactate(-)33), with the results of enantiomer enrichment comparable with literature [2]. See results table Tab. 1.

Tab.1: Pervaporation experiments results

AN-VImEt+L-Lactate40	17 % R(+)
SNCB6KIL5%	15 % S(-)
AN-VBCI-TPh(+)+L-Lactate(-)33	14 % R(+)

During pertraction experiments we find out, that kinetics of the pertraction significantly influence the enantiomer resolution what indicated that facilitated transport is employed.

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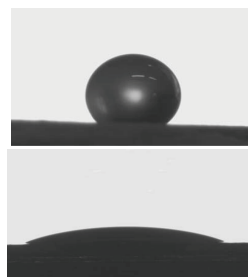
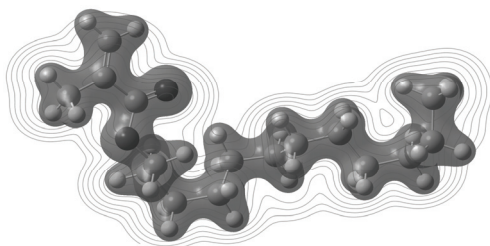
UTJECAJ POLIMERNOG ADITIVA MOTORNOG ULJA NA KONTAKTNI KUT MOČENJA METALA

INFLUENCE OF POLYMERIC ADDITIVE OF MOTOR OIL ON WETTING OF METALS

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Novi propisi vezani uz emisije štetnih plinova pridonijeli su razvoju novih motornih sustava (npr. EGR u dizelovim motorima) koji vrlo učinkovito smanjuju emisije NO_x plinova u atmosferu. Međutim, istodobno dolazi i do stvaranja veće količine nepoželjnih taloga u motornim uljima koji se mogu adsorbirati na površini motora i time uzrokovati niz nepovoljnih utjecaja. Da bi se to spriječilo, moderna motorna ulja moraju imati poboljšana disperzantna svojstva što se postiže dodavanjem aditiva s ugrađenom funkcionalnom skupinom na temelju dušika ili kisika. Uloga funkcionalne skupine jest da dispergira čestice taloga u ulju i/ili sprječava njihovo taloženje stvaranjem tankog površinskog filma na vitalnim dijelovima motora. Kako bi ustanovili interakciju između metalne površine motora i motornih ulja, u ovom radu ispitan je utjecaj sastava i koncentracije više različitih polimernih aditiva motornih ulja na kontaktni kut močenja tri različite čvrste podloge: ugljični čelik, nehrđajući čelik - inox i staklo. Aditivi na temelju stiren / *n*-alkil-metakrilat kopolimera sintetizirani su u baznom ulju s promijenjivim udjelom *N,N*-dimetilaminoetil metakrilata (DMAEM), monomera koji sadrži polarnu amino skupinu. Tako pripremljene 50 %-tne polimerne otopine, razrijeđene su na 1, 5 i 10 mas. % te im je određena močivost podloge mjerenjem kontaktnog kuta. Također je određena močivost i za 1 i 5 %-tne otopine komercijalnog poliolefinskog aditiva u ulju. S ciljem razumijevanja promjena Gibbsove energije, pomoću programske podrške Gaussian 09 i *ab initio* metode izračunate su optimalne geometrije i elektronske gustoće pojedinih monomera i polimernih segmenata.



Ustanovljeno je da se promjenom sastava i koncentracije aditiva, mijenja i kontaktni kut močenja mazivih ulja na ispitanim čvrstim podlogama. Povećanjem udjela DMAEM u aditivu, smanjuje se kontaktni kut odnosno površinska napetost mazivih ulja, a time i sadržaj slobodne površinske energije što za posljedicu ima bolje močenje i interakciju s podlogom.

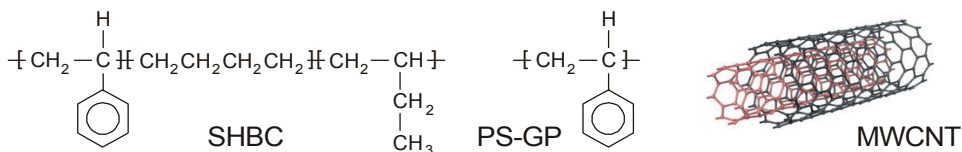
PRIGUŠIVANJE ZVUKA I VIBRACIJA KOMPOZITA NA TEMELJU STIREN-BUTEDIEN KOPOLIMERA SOUND AND VIBRATION DAMPING PROPERTIES OF COMPOSITES BASED ON STYRENE-BUTADIENE COPOLYMER

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Development of (nano) materials with new properties and structures is essential for further progress in modern technologies and fields of research and engineering. Aim of this work was to develop materials for application in the field of vibration and sound damping. Dynamic-mechanical and damping properties of polymer blends, comprised of PS-GP (general purpose polystyrene) and SHBC (styrene–hydrogenated butadiene copolymer), were investigated. Series of polymer blends with various PS/SHBC ratios were prepared by mixing of solutions of single polymers in toluene. Furthermore, composites with various weight fractions of multiwall carbon nanotubes (MWCNT) as filler were prepared by solution mixing, using high speed stirrer and ultrasonic bath. Mixtures were cast in PTFE molds and dried at 60 °C.



Obtained materials were characterized by dynamic-mechanical analysis (DMA) in order to determine glass transition temperature and primary viscoelastic functions (storage modulus, loss modulus, tan delta) and by differential scanning calorimetry (DSC) in order to confirm thermal phase transitions. Modified dynamic-mechanical analysis according to ISO 6721 (Oberst's method) was used to determine loss factor of material, which is a direct measure of capability of material to absorb energy of vibration and sound. Scanning electron microscopy was utilized to observe morphology of prepared polymer blends and composites. DMA results show glass transition temperature in a range between - 20 °C and - 10 °C for all prepared materials. Results of the Oberst's method show that maximum values of loss factor are obtained at temperature around -10 °C; as expected, energy absorption capability reaches its maximum around glass transition temperature of material. Also, it has been determined that with increase of the MWCNT content in composite, loss factor increases as well.

MODIFIKACIJA BITUMENA S REAKTIVNIM POLIMEROM BITUMEN MODIFIED WITH REACTIVE POLYMER

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Kontinuirano povećanje gustoće prometa dovelo je do šire uporabe polimerom modificiranog bitumena u cestogradnji. Već mali udio dodanog polimera kao modifikatora bitumena značajno mijenja njegova svojstva, pridonosi: smanjenju temperaturne osjetljivosti, trajne deformacije i poboljšanju otpornosti pri niskim temperaturama. Glavni problem modifikacije bitumena u uporabi predstavlja stabilnost na skladištenje. Pri visokim temperaturama dolazi do razdvajanja faza bitumena i polimera. Modifikacijom bitumena s reaktivnim polimerom dolazi do stvaranje kemijske veze između sastavnica bitumena i polimera, što pridonosi stabilnosti mješavine, odnosno otpornosti na skladištenje, kao i sprečavanje fazne separacije prilikom transporta i primjene. Cilj ovog rada je ispitati utjecaj reaktivnog polimera, etilen butil akrilat glicidil metakrilata (EBAGMA) prvenstveno na stabilnost polimerom modificiranog bitumena, PMB-a. Istraživanja uključuju i ispitivanja reoloških svojstava, primarne viskoelastične funkcije, čistih bitumena BIT 70/100 i BIT 50/70 te bitumena modificiranih s EBAGMA polimerom, Elvaloy AM i Elvaloy 4170 s različitim udjelom reaktivne funkcionalne skupine, GMA, odgovorne za stvaranje polimerne mreže kemijske prirode. Reološka svojstva provedena su dinamičkim smičnim reometrom u linearno viskoelastičnom području u temperaturnom intervalu od - 5 °C do 80 °C pri frekvenciji prometa od 10 rad/s što simulira prosječnu brzinu prometa od 75 km/h. Otpornost na trajnu deformaciju određena je iz viskoelastičnih funkcija, prema relaciji $G^*/\sin \delta$. Radi potpunije karakterizacije ispitivanja uključuju i standardne konvencionalne metode prema normama. Rezultati pokazuju da modifikacijom bitumena s reaktivnim polimerom koji sadrži veći udio reaktivne funkcionalne skupine, GMA, odgovorne za kemijsku reakciju, pridonosi izuzetnoj stabilnosti PMB-a bez fazne separacije. Reološka ispitivanja ukazuju na povećanje kompleksne viskoznosti, kompleksnog modula te smanjenje faznog kuta kao indikatora elastičnosti PMB-a. PMB pokazuje manju temperaturnu osjetljivost, bolju otpornost pri niskim temperaturama kao i veću otpornost na trajnu deformaciju.

**PRAĆENJE SIMULTANE SAHARIFIKACIJE I
FERMENTACIJE ŠKROBA IZ POLUČVRSTIH SIROVINA
DO MLIJEČNE KISELINE
MONITORING OF SIMULTANEOUS SEMI-SOLID STATE
SACCHARIFICATION AND FERMENTATION OF
STARCH FROM RAW MATERIALS TO LACTIC ACID**

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Starch containing raw materials represent preferable ingredients of more or less complex media to be used in sustainable biotechnological production of lactic acid. After upstream processing, prepared starch-based medium can adopt structure of suspension, gel, or semi-solid material with relatively low content of free liquid (water), as well as a combination thereof. Utilization of such heterogeneous media in bioprocess for lactic acid production requires additional efforts related to: adaptation of bioreactor construction and the medium mixing, definition of mass and energy transfer, selection of applicable analytical methods, their adaptation for bioprocess monitoring, *etc.* Several analytical methods were selected, adapted and tested for monitoring of Simultaneous Semi-Solid State Saccharification and Fermentation (S₅F) of starch to lactic acid. Suspension of corn grits in demineralized water that consisted of two easy-separable phases (liquid and semi-solid phase) was used as a minimal medium for direct production of D-/L-lactic acid by *Lactobacillus amylovorus* DSM 20531^T. Settling rate of corn grits particles, absorbance maxima and initial composition of heterogeneous medium were determined. During the S₅F the reduction of semi-solid phase portion and concentration of polymeric substrates in the two phases were followed by using customized analytical methods.

Keywords: bioprocess monitoring, simultaneous semi-solid state saccharification and fermentation, starch, raw material, direct lactic acid production, analytical methods

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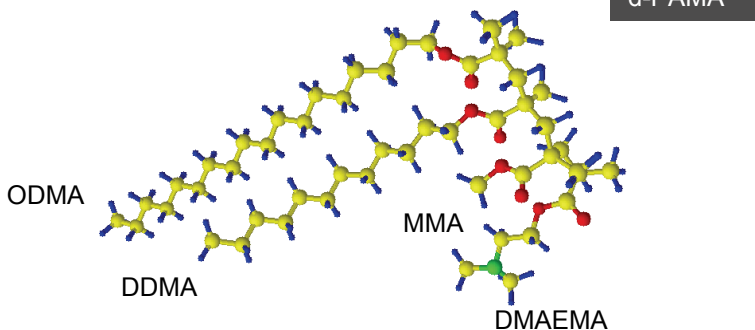
SINTEZA I KARAKTERIZACIJA DISPERZNIH PAMA ADITIVA I PRIMJENSKO-REOLOŠKA SVOJSTVA FORMULIRANIH MOTORNH ULJA SYNTHESIS AND CHARACTERIZATION OF DISPERSIVE PAMA ADDITIVES AND RHEOLOGICAL PROPERTIES OF FORMULATED MOTOR OILS

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U ovom radu naglasak je stavljen na istraživanje primjensko-reoloških svojstava multifunkcionalnog polimetakrilatnog aditiva u mineralnom baznom ulju koji uz poboljšanje indeksa viskoznosti i stiništa doprinosi i detergentno-disperznim svojstvima. Disperzni poli(alkil-metakrilatni) aditivi, d-PAMA, pripravljeni su radikalskom kopolimerizacijom metil-metakrilata, dodecil-metakrilata, oktadecil-metakrilata i dimetilaminoetil-metakrilata (DMAEMA, udjela 2, 5 i 10 mol. %) uz različite udjele prijenosnika lančane reakcije u baznom ulju SN-150 uz difunkcionalni peroksidni inicijator.



Sintetiziranim polimernim aditivima određena je raspodjela molnih masa kromatografijom isključenja po veličini, SEC, toplinska svojstva metodom diferencijalne pretražne kalorimetrije, DSC, toplinska postojanost u struji inertnog plina, N₂, i u struji zraka metodom termogravimetrijske analize, TGA. Primjensko-reološka svojstva određena su prema normiranim metodama: točka tečenja, viskoznost, indeks viskoznosti te smična stabilnost. Sve razrijeđene otopine polimera u baznom ulju pokazale su visoke vrijednosti kinematičke viskoznosti i indeksa viskoznosti (> 160). Ugradnjom DMAEMA u makromolekulu mijenjaju se molekulska međudjelovanja između polimernog aditiva i ulja, što rezultira znatno većim hidrodinamičkim klupkom polimernih molekula u usporedbi s nedisperznim aditivima metakrilatne osnove. Porastom volumena klupka povećava se viskoznost, a smanjuje smična stabilnost otopina, dok su stiništa usporediva.

REDUCTION AND OPTIMIZATION OF LOW TEMPERATURE SHIFT CATALYST FOR WATER GAS REACTION IN AMMONIA PRODUCTION

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In order to obtain additional quantities of hydrogen after the reforming reactions of natural gas and to protect the ammonia synthesis catalyst it is crucial to achieve and maintain the maximum possible activity of low temperature shift catalyst for conversion of water gas reaction during the lifetime of the same. For proper procedure of low shift catalyst reduction it is necessary to have except process equipment in the same time a reliable system for temperature measurements which will be effective for monitoring the exothermal curves through all catalyst bed layers. For efficiency evaluation of low shift temperature catalyst reduction and optimization of the same it is necessary at regular intervals determined the temperature approach to equilibrium and temperature profiles of individual layers by the help of „S“ and „Die off“ temperature curves. According to the obtained data it can be on satisfactorily manner conduct the optimally increasing of the inlet temperature in the low temperature shift catalyst, in order to maximally extend the lifetime of the catalyst and to achieve the optimum equilibrium for conversion of water gas. This paper represents a methodology for reducing the low temperature shift catalyst and developed system for monitoring the individual layers of the catalyst in order to achieve the minimum possible content of the carbon monoxide at the exit of reactor. The developed system for temperature monitoring through catalyst layers provide the proper procedure for reduction and adjustment of optimum process working conditions for catalyst by the continuous increase of the reactor inlet temperature. With the applied system it can be achieved the maximum catalytic activity and the ability to predict the catalyst performance which can be the basis for proper decision on its timely replacement and significantly reduction of the production costs.

Key words: ammonia, low temperature shift conversion, reduction, temperature, water gas

5-DIJELNI KINETIČKI MODEL KATALITIČKOG KREKIRANJA HIDRODESULFURIZIRANOG PLINSKOG ULJA 5-LUMP KINETIC MODEL OF HYDROTREATED GAS OIL CATALYSTIC CRACKING

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U radu je ispitan utjecaj promjene temperature katalitičkog kreiranja na konverziju, prinose i raspodjelu produkata katalitičkog kreiranja dobivenih iz hidrodesulfuriziranih plinskih ulja. Na osnovi predodžbe o reakcijskom mehanizmu katalitičkog kreiranja te provjere s eksperimentalnim rezultatima dobivenim testom mikroaktivnosti, predložen je 5-dijelni kinetički modeli kreiranja hidrodesulfuriziranih plinskih ulja. Na temelju teorijskih razmatranja i eksperimentalnih rezultata izveden je model cijevnog reaktora s nepokretnim slojem katalizatora u MAT aparaturi na osnovi pretpostavke o neizotermnom i nestacionarnom radu. Kinetička analiza provedena je pomoću sekvencijalne metode, dok su kinetički parametri procijenjeni Nelder-Mead-ovom metodom. Rezultati dobiveni kinetičkim modeliranjem uspoređeni su s eksperimentalno dobivenim podacima u odnosu na korištenu sirovinu i temperaturu reakcije. Rezultati simulacije mogu poslužiti kao osnova za predviđanje prinosa produkata u komercijalnim FCC jedinicama te u laboratorijskim uređajima.

Ključne riječi: test mikroaktivnosti, kinetika katalitičkog kreiranja, kinetički modeli, modeliranje MAT reaktora

**UTJECAJ UVJETA EKSTRAKCIJE NA ODREĐIVANJE
UDJELA LIGNINA U RAZLIČITIM UZORCIMA
BIOMASE**
**EFFECT OF EXTRACTION PROCEDURE ON LIGNIN
DETERMINATION IN DIFFERENT BIOMASS SAMPLES**

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The numerous methods have been developed to quantitatively determine the amount of lignin in different type of biomass. Many of them are based on using mineral acid to hydrolyse carbohydrate in cell wall of the biomass sample whereat the solid residue represents the acid-insoluble lignin, which can be gravimetrically measured. These methods mostly require antecedent preparation of sample within the meaning of removing potentially interfering compounds as inorganic and nitrogen materials, non-structural sugars, phenols, fats, sterols, waxes and chlorophyll, among others. Solid-liquid extraction is most often method used for the removal of components that can interfere with the down stream analysis in biomass sample, in general. The different types of biomass involve various extraction procedures. So, the aim of this work was to study the effect of two-step and one-step extractions with different solvents on determined amount of acid-soluble and acid-insoluble (Klason) lignin in some sample of sawdust as well as in beet residue after saccharose production process. The obtained results indicate the importance of extraction parameters (extraction time, solvent, number of steps) on removal of extractives and determination of total lignin with regard to biomass type.

**ODREĐIVANJE PSEUDOKAPACITIVNIH SVOJSTAVA
ELEKTROKEMIJSKI DEPONIRANOG MnO_2
DETERMINATION OF PSEUDOCAPACITIVE
PROPERTIES OF ELECTROCHEMICALLY
DEPOSITED MnO_2**

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U ovom radu proučavano je pseudokapacitivno ponašanje MnO_2 dobivenog elektrokemijskim putem (potencijostatski) iz otopine MnSO_4 . U tu svrhu pripravljena su 3 sloja različite debljine kako bi se uvidjelo postoji li utjecaj debljine sloja na pseudokapacitivnu reakciju MnO_2 . Svi dobiveni uzorci ispitivani su cikličkom voltametrijom uz praćenje odziva elektrokemijske kvarc kristalne nanovage (EQCN). Uzorci su također ispitivani i kombiniranim tehnikama kvarc kristalne nanovage, kronoamperometrije te cikličke voltametrije. Dobiveni rezultati ukazuju da je ponašanje svih slojeva slično i da pokazuju pseudokapacitivno ponašanje, a pseudokapacitivna reakcija uključuje kombinirani ionski transport natrija i različito hidratiziranih protona. Istraživanje daje doprinos razumijevanju redoks reakcije MnO_2 kao pogodnog materijala za primjenu u superkondenzatorima.

PREHRAMBENA TEHNOLOGIJA I BIOTEHNOLOGIJA
FOOD TECHNOLOGY AND BIOTECHNOLOGY

THE IMPACT OF GRAPE SEEDS AND POMACE ON DEOXYNIVALENOL DEVELOPMENT IN WHEAT GRAIN

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Mycotoxins are toxic chemical products formed as secondary metabolites by a few fungal species that colonize crops and contaminate them with toxins in the field or after harvest. They are produced during growth and multiplication of fungi when microecology conditions are favourable. In order to prevent and inhibit the development of fungal preservatives are often added to moist cereals. In this paper we studied the effect of natural extracts derived from grape seeds (GSE) and grape pomace (GPE) on the development of deoxynivalenol (DON) in storage wheat. The results show that DON production was significantly reduced by the presence of natural extracts. The wheat grains treatment with GPE has as effect the higher decreases recorded in DON content ranged between 5.46 to 49.19 %. The maximum decrease using natural antioxidants was recorded after 28 days of treatment with GPE at 500 ppm level. Due to their remarkable antioxidant properties, the extract obtained from wine industry by-products are recommended as natural additives in food industry and are able to provide fungicidal and fungistatic protection and control of DON accumulation in wheat grain at least similar as synthetic antioxidant butylated hydroxytoluene (BHT).

Keywords: deoxynivalenol (DON), wheat grain, grape seed, grape pomace

OPTIMIZATION OF SOLID-LIQUID EXTRACTION OF ANTIOXIDANTS AND TOTAL SUGAR FROM BLACK MULBERRY FRUIT BY RESPONSE SURFACE METHODOLOGY

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The aim of this study was to examine the influence of solvent composition (ethanol/water, 40–80 %, by volume), temperature (40–80 °C) and time (20–60 min) on the extraction yield of phenolic compounds, flavonoids, sugars and antioxidant activity of black mulberry (*Morus nigra* L.) fruit. Experimental values of total phenolic content were in the range from 15.38 to 18.43 mg of chlorogenic acid equivalents per g of dry extract and total flavonoids in the range from 7.74 to 12.33 mg of rutin equivalents per g of dry extract. Antioxidant activity expressed as IC₅₀ value was in the range from 0.0237 to 0.0353 mg of mulberry extract per mL. Total sugar content was in the range from 4.655 to 5.022 mg per g of dry extract. Response surface methodology was used to determine the optimum extraction conditions and to investigate the effect of different variables on the observed properties of mulberry fruit extract. Optimal conditions within the experimental range of the studied variables were 58.7 %, 58.1 °C and 46.9 min. The experimental values agreed with those predicted, thus indicating suitability of response surface methodology in optimizing the investigated extraction conditions.

Keywords: black mulberry fruit, response surface methodology, phenolics, flavonoids, DPPH, total sugar content

KARAKTERIZACIJA BARIJERNIH SVOJSTAVA MODIFICIRANE POLIETILENSKE FOLIJE CHARACTERIZATION OF BARRIER PROPERTIES OF MODIFIED POLYETHYLENE FOIL

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Fleksibilni ambalažni materijali koji se koriste u prehrambenoj industriji najčešće su sastavljeni od jednog ili više slojeva. Jedan od ključnih parametara pri odabiru materijala su njegova barijerna svojstva, koja će štititi upakirani sadržaj od utjecaja kisika, vodene pare ili svjetla iz okoliša kao i gubitak osjetljivih komponenti iz proizvoda kroz ambalažu. Cilj ovog rada bilo je ispitivanje barijernih svojstava polimernih materijala. Istraživana je propusnost modificirane polietilenske (PE) folije s različitim udjelom aditiva (5 %, 10 %, i 15 %) iz skupine antioksidansa. Istraživana je propusnost modificiranih PE folija na kisik, dušik i ugljikov dioksid kod različitih temperatura (4 °C; 15 °C; 20 °C; 30 °C; 40 °C i 50 °C). Određivani su koeficijenti difuzije (D), permeacije (P) i topljivosti (S) plinova u istraživanim PE uzorcima. Temperaturna ovisnost parametara propusnosti (koeficijent permeacije, $\ln P$ i koeficijent topljivosti, $\ln S$) plinova prikazana je Arrheniusovim grafičkim prikazom. Računata je energija aktivacije za permeaciju i toplinu sorpcije. Simulacija utjecaja rukovanja polimernim materijalom provedena je primjenom različitih ciklusa savojnog naprezanja. Utjecaj propusnosti plinova te ciklusa savojnog naprezanja, na istraživane PE uzorke, određeni su FT-IR spektroskopijom.

TRIACYLGLYCEROLS COMPOSITION OF SOYBEAN OIL FRACTIONS OBTAINED WITH SUPERCRITICAL CO₂

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Hexane is widely used as solvent in the processing of vegetable oils; however, the use of organic solvents causes the environmental problems which can be solved by alternative extraction procedures, such as supercritical extraction with CO₂. Soybean oil fractionation with supercritical CO₂ at different extraction process conditions was performed. The influence of pressure (300–500 bar), temperature (40–60 °C), CO₂ flow rate (0.194–14.125 kg/h) and particle size (0.238–1.059 mm) were investigated. Soybean oil was fractionated into few fractions collected at different time intervals during extraction. The concentration of triacylglycerols in different fractions of soybean oil obtained at different extraction process conditions was determined. Triacylglycerols were analyzed by reversed phase high performance liquid chromatography with refractive index detector and identified by comparing their retention time to standards. The triacylglycerols composition of soybean oil obtained with supercritical CO₂ was compared with the soybean oil extracted by n-hexane. By selecting the relevant process conditions of supercritical extraction, as well as by fractionation, it is possible to obtain soybean oil with different mass concentrations of triacylglycerols. The obtained concentration of main triacylglycerols of soybean oil was as follows: trilinolein (16.34–23.62 %), dilinoleolein (14.61–17.07 %), dilinoleopalmitin (10.86–16.82 %), and linoleoleopalmitin (11.82–15.44 %), depending on extraction conditions.

Keywords: triacylglycerols, fractions, soybean oil, supercritical CO₂ extraction

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THE INFLUENCE OF VARIETY AND AMOUNT OF SUGAR IN THE FRUIT ON THE QUANTITY AND QUALITY OF FIG BRANDY

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The fig (*Ficus carica* L.) is one of the oldest domesticated fruit species. The interest for its cultivation in Croatian region Istria is growing, due to the wish to achieve the diversity of agricultural activities. Together with olives and grapevine, fig is a recognizable symbol of the Mediterranean region. It is important ingredient used for culinary and cosmetic purposes. Fig fruit can be consumed fresh or dried, or it can be used processed in many ways. One of them is a brandy prepared from fresh figs. Quality of fig brandy is influenced by many factors, namely, climate and soil characteristics, fig varieties and technological characteristics of manufacturing process. The aim of this work was to study the influence of fig variety and the amount of sugar in the fruit on the quantity and the quality of the fig brandy. The brandy was produced using seven different fresh fig varieties (*Bružetka bijela*, *Bružetka crna*, *Fico della Madonna*, *Grčka crna*, *Petrovača crna*, *Šaraguja* and *Zimica*). The quality of fig brandy was assessed by laboratory (densitometry, titrimetry and gas chromatography) and sensory (DLG, positive number method) analysis. Fig variety had a significant influence on quality of brandy.

Keywords: fig, brandy, quality, quantity

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INFLUENCE OF SUGAR ADDITION AND PH ON PIGMENT STABILITY AND COLOUR OF FROZEN RED BEET PUREE

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In this study influence of glucose, fructose and sucrose (3, 5 and 7 %), and pH (3 and 5), with the addition of ascorbic and citric acid on betacyan pigment stability and colour of red beet puree before freezing, and after 1 and 6 months of storage at - 18 °C, was investigated. To study the thermal properties of red beet puree differential scanning calorimetry was used. Enthalpy of melting (ΔH), onset (T_o) and melting peak temperatures (T_p) were determined. The results showed the highest stability of betacyans when ascorbic and citric acid were added (pH 3 and 5), and the lowest stability when glucose was added (3, 5 and 7 %). The highest colour change (ΔE) during storage was observed with glucose addition, and lowest with fructose addition. Enthalpy of melting (ΔH) decreased when sugars were added, and when the amount of sugar was higher, while the samples with addition of acids had ΔH values from 238.54 to 247.45 Jg⁻¹. Red beet puree showed excellent stability during 6 months of storage, especially with addition of acids (pH 3 and 5), which is very important for potential application of red beet as a source of natural food colorant in certain products.

Keywords: red beet, betacyans, sugar, colour, freezing.

OCHRATOXIN A IN HOMEMADE SAUSAGES PRODUCED FROM TREATED PIGS

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Ochratoxin A (OTA) is a natural contaminant of cereals and feed, often present in meat and offal of farm animals and products of animal origin. The aim of this study was to determine the OTA residues in different types of homemade sausages produced from pigs after subchronic treatment with OTA. Treated group of animals ($n = 5$) were administered a dose of 300 µg OTA/kg of feed for a period of 30 days while the other animals ($n = 5$) were not treated and served as control group. Cooked (liverworts, pudding and pate) and dried (kulen, homemade sausage and Slavonian salami) sausages were home-made according to different traditional recipes from appropriate raw materials. Residue concentrations of OTA in these products were determined by liquid chromatography with fluorescent detection (HPLC-FD). The highest concentrations of OTA in finished products were in blood sausages (12.82 µg/kg), followed by liverworts (12.17 µg/kg) and pate (7.92 µg/kg) while the concentrations of OTA in dried sausages were significantly lower and varied from 5.19 µg/kg to 5.75 µg/kg. The study showed that subchronic exposure of pigs to OTA from feed leads to accumulation of OTA residues in offal and edible carcass parts. The concentration of OTA residues in produced sausages is directly dependent on the degree of contamination of raw materials and their content in final products.

**POVEZANOSTI REOLOŠKIH I SENZORSKIH
SVOJSTAVA MLIJEČNIH ČOKOLADA
RELATION RHEOLOGICAL AND SENSORY
PROPERTIES OF MILK CHOCOLATES**

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Melted chocolate is a suspension composed of sugar, solid parts of cocoa beans and milk powder particles dispersed in fatty continuous phase made of cocoa butter and other added fats (milk fat, fat replacements). Type and share of each compound affects rheological properties of chocolate, and thus quality and sensory acceptance of finished product (mouth solubility, taste, surface gloss, braking).

The object of this research was to determine rheological and sensory properties of six different milk chocolates, and what is a relation between those properties. Rheological properties were measured by rotation rheometer (Thermo Haake VT 550 Digital Rheometer). Rheological parameters were calculated by Casson model. Sensory evaluation did seven trained analyzers. Results showed direct relation between rheological and sensory properties. Chocolates with lower values of rheological parameters (plastic viscosity and yield stress) had higher grades for solubility, while chocolates with higher values of rheological parameters had higher grades for properties of breakage.

Key words: chocolate, rheological properties, sensory properties

UTJECAJ PROCESIRANJA NA SADRŽAJ POLIFENOLA I ANTIOKSIDACIJSKU AKTIVNOST JABUKA IMPACT OF PROCESSING ON POLYPHENOLS CONTENT AND ANTIOXIDANT ACTIVITY OF APPLE

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U posljednje vrijeme znanstvenici i proizvođači pokazuju veliki interes za namirnice bogate polifenolima. Glavni razlog je taj što polifenoli imaju važnu ulogu u prevenciji različitih bolesti. Polifenolima se pripisuje i antioksidacijsko svojstvo koje je uglavnom posljedica njihovog redoks svojstva koje im omogućuje djelovanje kao redukcijsko sredstvo, donor vodika, vezanje slobodnih radikala, ali i inhibicije enzima koji mogu povećati oksidacijski stres. Cilj istraživanja je bio utvrditi utjecaj procesiranja (zamrzavanja, sušenja) te skladištenja (šest mjeseci) na sadržaj polifenola i antioksidacijsku aktivnost nekih sorata jabuka. Udio ukupnih polifenola u sve tri sorte jabuka je bio najveći u kori jabuka. Sorte jabuka Gold Rush i Fuji su imale najveći udio ukupnih polifenola u kori (sorta Gold Rush 3.53 +/- 0.059 g/kg, sorta Fuji 3.28 +/- 0.082 g/kg). Najmanji gubitak polifenola nakon zamrzavanja je zabilježen u jabukama sorte Gold Rush (45 % pulpa, 40 % kora + pulpa i 24 % kora). Nakon sušenja najmanji gubitak polifenola je također zabilježen u jabukama sorte Gold Rush (58 % pulpa, 35 % kora + pulpa i 10 % kora). Antioksidativna aktivnost (AA) mjerena DPPH i ABTS metodom je bila najveća u svježim uzorcima i opadala je tijekom skladištenja jabuka, kao i njihovim procesiranjem.

**PRIMJENA KEMOMETRIJSKE ANALIZE NIR
SPEKTARA U UTVRĐIVANJU PATVORENJA
JESTIVIH ULJA
USE OF CHEMOMETRIC ANALYSIS OF NIRS DATA IN
DETECTION OF ADULTERATION OF EDIBLE OILS**

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In this study edible oils were analysed in order to identify a possible use of near-infrared spectroscopy (NIRS) in detection of their adulteration. NIR spectra of five edible oils (three types of olive oil, pumpkin oil and vegetable oil) and oils with addition of vegetable oil in different proportions (5, 10, 15 and 20 %) simulating adulteration were recorded in the range (899–1699 nm, 8495–4495 cm^{-1} , respectively) to observe vibrations of –CH and –OH bonds. The main features of the spectra are the absorption bands at 904–922 nm which are related to the 3rd CH overtone and 2nd overtone of the OH stretch of H₂O and a combination of stretch and determination of the OH group and bands, and at 1675 and 1699 nm which are related to the first overtone of the CH stretch and in H₂O, respectively. Used principle component analysis showed a high level of disjunction of observed pure oil samples and oil samples according to the diluted level using the first two components (PC1+PC2 > 90 %). The non-destructive analytical method – NIRS has shown the potential in determination of different edible oils with possibility of determination of adulteration level. This study has shown that NIRS combined with chemometrics is a useful tool in edible oil quality control.

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UTJECAJ KLIMATSKIH ČIMBENIKA NA KAKVOĆU VINA SOTRE MUŠKAT ŽUTI U VINOGORJU KUTJEVO IMPACT OF CLIMATIC FACTORS ON THE QUALITY OF WINE VARIETY MUSKAT IN THE KUTJEVO VINEYARD

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Muškat žuti je nova sorta grožđa u Vinogorju Kutjevo, a od 1998. je uvrštena u registar dopuštenih sorata. Budući da se radi o novoj sorti u vinogorju, kroz četiri godine prikupljeni su parametri dinamike dozrijevanja grožđa, opterećenje trsova, urod te količina sladora i ukupnih kiselina u grožđu i moštu. U sve četiri godine berba se odvijala tako da se u redovnoj berbi skidalo oko 60% uroda, a ostatak je bran kasnije kao izborna berba kada bi grožđe imalo minimalno 105 °Oechsle. Fermentacija se odvijala u tankovima od inoxa veličine 1000 litara uz dodatak selekcioniranih kvasaca. Temperatura mošta tijekom fermentacije iznosila je 18 °C. Nakon fermentacije vino je bistreno pentagelom, filtrirano na pločastom fileru te napunjeno u boce preko mikrofiltera. Nakon izvršenih kompletnih kemijskih i organoleptičkih analiza, vidljive su karakteristike sorte muškat žuti, s posebnim osvrtom na odnose kiselina i šećera u moštu. Može se reći da je Muškat žuti kao izrazito aromatična sorta vrlo zahtjevnja i ukoliko se pravilno ne ograniči prinos, u periodu od svega nekoliko dana tijekom tehnološke zrelosti grožđa ne izvrši berba, te izvrši samo jedna kriva manipulacija u kasnijoj obradi vina, izostaje specifičan aromatski karakter sorte.

**UTJECAJ DJELOMIČNE DEFOLIJACIJE NA KEMIJSKI
SASTAV MOŠTA KULTIVARA SAUVIGNON
BIJELI (*Vitis vinifera* L.)
INFLUENCE OF PARTIAL DEFOLIATION ON
CHEMICAL COMPOSITION OF THE MUST VARIETY
SAUVIGNON BLANC (*Vitis vinifera* L.)**

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Djelomična defolijacija vinove loze podrazumijeva prorjeđivanje ili uklanjanje bazalnih listova u zoni razvoja grozdova kako bi se osigurala veća prozračnost, bolji pristup svjetla te samim tim smanjila mogućnost zaraze sivom plijesni i postigla bolja obojenost bobica. Cilj ovog istraživanja bio je utvrditi utjecaj različitog stupnja i termina djelomične defolijacije u uvjetima Vinogorja Kutjevo na kemijski sastav mošta kultivara Sauvignon bijeli, prateći parametre sadržaja šećera i ukupne kiselosti te vinske, jabučne i limunske kiseline u moštu. Pokus je postavljen kao slučajni blokni raspored u četiri repeticije sa sljedećim tretmanima: bez odstranjivanja listova, odstranjena četiri bazalna lista nakon cvatnje, odstranjeno osam bazalnih listova nakon cvatnje, odstranjeno četiri bazalna lista početkom faze šare grožđa i odstranjeno osam bazalnih listova početkom faze šare grožđa. Rana i kasna djelomična defolijacija osam bazalnih listova utjecala je na smanjenje sadržaja šećera u 2005. godini. Rana djelomična defolijacija osam bazalnih listova u nepovoljnim klimatskim uvjetima utjecala je na smanjenu ukupnu kiselost. Djelomična defolijacija nije utjecala na sadržaj vinske kiseline u moštu, a sadržaj jabučne i limunske kiseline u slučaju rane i kasne djelomične defolijacije osam bazalnih listova značajno je manji u klimatski nepovoljnijoj godini.

THE INFLUENCE OF YEAR AND LOCATION ON POLYPHENOL AND ANTHOCYANIN CONTENT IN SOUR CHERRY CULTIVARS

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Sour cherry is an important fruit in Croatian orchards because its products are very popular within food industry. The products, such as jams, juice concentrates, frozen sour cherries, alcoholic drinks and other, are rich in antioxidants. The aim of this study was to determine how different locations and years influence polyphenol and anthocyanin content in fruits of different sour cherry cultivars. Fruits of six sour cherry genotypes were harvested in two locations (Osijek and Zadar) over three consecutive but climate different years (2009, 2010 and 2011). The content of polyphenols and anthocyanins was determined spectrophotometrically. Analysis of variance showed that year significantly influenced polyphenols and anthocyanins content. 2010 was the best year with 932.32 mg of gallic acid/100g fresh weight of polyphenols and 483.10 mg of cyanidin-3-glucoside/100g of fresh weight of anthocyanins in average. The results of one-way ANOVA indicated that location did not influence the accumulation of polyphenols and anthocyanins in sour cherry fruits. According to content of polyphenols and anthocyanins, cvs. Maraska and Rexelle appear to be the best source of bioactive compounds over the investigated genotypes.

Keywords: anthocyanins, climate, polyphenols, season, sour cherry

ANTIOXIDANT ACTIVITY AND TOTAL PHENOLIC CONTENT OF SWEET CORN HYBRIDS DURING MATURATION

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Phenolics are the most widespread secondary metabolites in the plant and have taken much attention as potential natural antioxidants in terms of their abilities to act as efficient radical scavengers and metal chelators. The plant material used in this study were ten early maturing *su* sweet corn hybrids, created at the Agricultural institute Osijek. The field trial was set up in 2009 and included two replicates of hybrids arranged in a randomized complete block design. Cobs were hand harvested 17, 19, 21, 23 and 25 day after controlled pollination. Total phenols and antioxidative activity were determined spectrophotometrically, after ultrasound extraction of lyophilized sweet corn grain with acidified methanol.

Significant difference between sweet corn hybrids and harvest date for both investigated traits was found. Results revealed that during maturation of sweet corn grains, total phenolic content decreased whereas the reverse was found for antioxidant activity determined by DPPH assay. The highest amount of total phenolic was observed on the first day of harvest for all hybrids, and for the Os 244 *su* hybrid it was 372.68 mg of gallic acid equivalents/100g. The maturation resulted in an increase of antioxidant activity up to 38% in relation to the value determined in the first harvest date.

PROIZVODNJA HEKSANALA U MIKROREAKTORU HEXANAL PRODUCTION IN THE MICROREACTOR

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One of the most interesting pharmaceutical, agrochemical and aroma compounds are so called “green notes”. Hexanal is a part of that group. Several processes for the production of hexanal that are based on fermentation, extraction from plants and enzyme-catalyzed reactions have been described. However, due to low yields, formation of unwanted by-products and large quantities of waste, traditional methods cannot provide a sufficient amount of hexanal [1]. Combination of microreactor technology and biotransformation could be a new solution for the production [2,3]. Large surface to volume ratio, excellent mass and heat transfer, shorter residence time, smaller amount of reagents, catalyst and waste products comparing to equivalent bulk reactions, laminar flow, effective mixing and better process control, small energy consumption and less environmental impact are just some of the microsystem advantages [4]. Implementation of microreactor technology for hexanal production is investigated in this study. Microreactors of different materials, e.g. glass and polytetrafluoroethylene (PTFE), suspended and immobilized enzyme alcohol dehydrogenase (ADH) isolated from baker yeast, and suspended and immobilized permeabilized yeast cells were used for hexanal production on microscale. Conversion of approximately 80 % for residence time of 72 s was observed in experiment with suspended ADH. For all investigated systems reaction kinetics was estimated and corresponding mathematical models were developed. Finally, the model prediction results were proven and verified on a set of independent experiments performed in a microreactor.

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POLIFENOLI I ANTIOKSIDACIJSKA SVOJSTVA PIVA TIJEKOM SKLADIŠTENJA POLYPHENOLS AND ANTIOXIDANT PROPERTIES OF BEER DURING STORAGE

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Beer is unstable product that is involved in series of chemical, physical and sensorial transformations during its shelf life. Maintaining beer quality through the various stages of maturation, distribution and shelf storage remains an extensive challenge [1]. Beer is beverage obtained through alcoholic fermentation of malt wort, usually made of barley, which could be partially substituted with other cereals, such as corn or wheat. It can be considered as a good source of polyphenols derived both from malt and hop. Beer polyphenols are crucial for foam maintenance, colloidal stability and shelf-life of beer [2]. This study evaluated the oxidative profile of four different types of Croatian lager beer (three pale lager and one dark) submitted to a forced aging process (5 days at 40 °C) and aging at room temperature (4 months at 20-22 °C). Beer samples were tested using four different spectrophotometric assays for antioxidant capacity: total polyphenol content, DPPH free radical scavenging, reducing power and copper(II)-chelating activity. The concentration of total polyphenols in dark beer was 463 mg/L and between 354 and 410 mg/L in pale lager beers, respectively. Results showed no changes in total polyphenol content and antioxidant capacity during forced aging process. Beers aged at room temperature showed a decrease in their polyphenol content and antioxidant capacity. All samples exhibited significant antioxidant properties, which were strongly correlated with the total polyphenol content of the beers.

Keywords: Beer, polyphenols, antioxidant capacity, aging, storage

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UTJECAJ VLAŽNOSTI I GRANULACIJE KUKURUZNE KRUPICE NA SVOJSTVA EKSTRUDATA INFLUENCE OF MOISTURE CONTENT AND PARTICLE SIZE OF CORN GRITS ON EXTRUDATES PROPERTIES

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Extrusion is a modern procedure for processing different types of raw materials and is used for production a wide range of food products (snack products, pasta, textured proteins...), as well as to modify the properties of different raw materials, mostly flour for biscuit and bakery industry, and for starch modification.

Corn grits is a basic raw material of different extruded food products, and therefore the aim of this research was to determine the effect of moisture content (15 % and 20 %) and particle size of corn grits (*Specijal* and *Resli*) on the properties of extruded products.

Grits were extruded on the laboratory single screw extruder Brabender 19/20 DN, at temperature profile 135/170/170 °C, using screw with compression ratio 4:1 and die with 4 mm diameter. Physical, rheological and thermophysical properties of the obtained extrudates, and starch damage were determinates.

The results showed that higher moisture content decreased the expansion ratio and fragility, but increased bulk density and hardness of extrudates, regardless of granularity. Properties of corn grits viscosity were significantly changed by extrusion, with more pronounced effect in grits extruded with lower moisture content, in which starch damage was also significantly higher.

Key words: extrusion, corn grits (*Specijal*, *Resli*), moisture content

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ISOLATION AND CHARACTERIZATION OF *STAPHYLOCOCCUS AUREUS* ISOLATED FROM UNPASTEURIZED MILK IN KOSOVO

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Staphylococcus aureus is a common causative agent of bovine mastitis in dairy animals. The aim of this work was to investigate the incidence of *Staphylococcus aureus* isolated from unpasteurized milk and milk products in Kosovo. The prevalence of *Staphylococcus aureus* was studied among 900 samples of un-pasteurized milk and milk products. Isolates were identified by gram stains, tests for coagulase, the API staph system and Multi-Locus-Sequencing-Typing (MLST). The result shows that 15.5 % of total samples were with coagulase-positive of *Staphylococcus aureus*. Analysis of the results obtained in the current work gives the recommendation for the public health inspectors to properly examine the conditions during production, storage and commercialization of all products made with unpasteurized milk.

Key words: *Staphylococcus aureus*, unpasteurized milk and milk products.

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UČINAK VRSTE I KONCENTRACIJE INHIBITORA NA SUŠENJE JABUKE

THE EFFECT OF VARIETY AND INHIBITOR CONCENTRATION ON THE DRYING OF APPLE

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Sušenje je jedan od najstarijih, ali još uvijek vrlo često korištenih načina konzerviranja prehrambenih proizvoda. Posebno se često koristi za voće i povrće. Problem kod sušenja predstavlja gubitak nekih važnih sastojaka, kao i degradacija pojedinih senzorskih svojstava. To se posebno odnosi na boju. Zbog toga se kao priprema voća za sušenje koriste i metode koje će spriječiti promjenu boje, odnosno posmeđivanje. Vrlo često se u tu svrhu koriste različite kiseline, blanširanje, šećer i sol kojima se tretiraju komadi voća prije sušenja. Cilj ovog rada bio je utvrditi kako tretiranje pojedinim inhibitorima različitih koncentracija (limunska i askorbinska kiselina u koncentracijama od 3 i 5 % i otopina šećera u koncentraciji od 1 i 3 %) utječu na očuvanje boje i sprečavanje posmeđivanja osušenih jabuka. U netretiranoj jabuci i uzorcima nakon tretiranja i sušenja je određen kemijski sastav (količina vode, odnosno suhe tvari, ukupnih, topljivih i netopljivih, šećera, ukupnih kiselina i pektinskih tvari). Na osnovu dobivenih rezultata moglo se zaključiti da je najbolji učinak na sprečavanje posmeđivanja jabuka imala 3 i 5 %-tna otopina askorbinske kiseline, a najslabiji 1 i 3 %-tna otopina šećera.

Ključne riječi: jabuka, sušenje, inhibicija, posmeđivanje

UTJECAJ EKSTRUZIJE NA POLIFENOLNE SPOJEVE I BOJU BRAŠNA I KEKSA

INFLUENCE OF EXTRUZION ON POLYPHENOL COMPOUNDS AND COLOUR OF FLOUR AND COOKIES

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Ekstruzija je jedna od novijih i perspektivnih načina obrade koji se koristi u prehrambenoj industriji. Ima višestruku ulogu: visoka temperatura i tlak koji se primjenjuju u toku procesa dovode do promjene sastojaka, prije svega proteina i škroba, a također se mijenjaju i organoleptička svojstva, prije svega tekstura. Ekstruzija utječe i na poboljšanje probavljivosti proteina i prehrambenih proizvoda.

Cilj ovog rada bio je utvrditi kako ekstruzija utječe na ukupne polifenolne spojeve u brašnu i keksima koji su od tog brašna napravljeni, te na boju gotovih proizvoda. Prema očekivanjima, količina polifenola se u brašnu smanjila nakon ekstruzije, kao i u svim vrstama keksa u kojima je korišteno ekstrudirano brašno. Kada je u pitanju boja vidljiva je razlika kod ekstrudiranog brašna i keksa napravljenih od tog brašna, pa se može zaključiti da je ekstruzija znatno utjecala i na promjenu boje kako brašna tako i keksa.

Ključne riječi: ekstruzija, brašno, keks, polifenolni spojevi.

**INTERLABORATORIJSKO ISPITIVANJE *E. coli*
I UKUPNIH KOLIFORMA PRIMJENOM MEMBRANSKE
FILTRACIJE U LABORATORIJSKI
PRIPREMLJENOJ VODI
INTERLABORATORY TESTING OF *E. coli* AND TOTAL
COLIFORMS BY MEMBRANE FILTRATION IN
LABORATORY PREPARED WATER**

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Prema modelu "Proficiency progama", FEPAS (međulaboratorijsko uspoređivanje), u kojem Podravka uspješno sudjeluje od 2005. godine, već treću godinu zaredom provodi se interlaboratorijsko ispitivanje *E. coli* i ukupnih koliforma primjenom membranske filtracije u vodi pripremljenoj u laboratoriju u skladu s prethodno utvrđenim uvjetima. Cilj interlaboratorijskog ispitivanja je utvrđivanje osposobljenosti laboratorija za provođenje određenih ispitivanja ili mjerenja kao i za uspoređivanje novih metoda ispitivanja. Provođenje interlaboratorijskog ispitivanja pruža laboratorijima objektivnan način za ocjenjivanje i prikazivanje pouzdanosti rezultata ispitivanja do kojih dolaze uspoređivanjem rezultata ispitivanja iz dva ili više laboratorija. U ovom radu prikazani su rezultati ispitivanja parametara zdravstvene ispravnosti, prema z-vrijednostima u laboratorijski pripremljenoj vodi (namjerno kontaminiranoj mikroorganizmima) između dva laboratorija. Rezultati ispitivanja ukazuju da je osposobljenost oba laboratorija zadovoljavajuća te da je potrebno kontinuirano provoditi interlaboratorijsko ispitivanje s ciljem osiguranja kvalitete rezultata ispitivanja i dokazivanja vjerodostojnosti rezultata.

Ključne riječi: interlaboratorijsko ispitivanje, voda, *E. coli*, ukupni koliformni, membranska filtracija

**OKSIDATIVNA STABILNOST BILJNIH ULJA I NJIHOVIH
MJEŠAVINA TIJEKOM ZAGRIJAVANJA PRI
TEMPERATURAMA PRŽENJA
OXIDATIVE STABILITY OF EDIBLE VEGETABLE OILS
AND THEIR MIXTURES DURING HEATING AT FRYING
TEMPERATURES**

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The scope of this study is the assessment of oxidative stability and quality of vegetable oils and vegetable oil mixtures at different temperatures and times of heating. The test was carried out with extra virgin olive oil (EDMU), rapeseed oil (RU), a mixture of rapeseed, sunflower and corn oil (RSKU) and a mixture of rapeseed oil, extra virgin olive oil, sunflower and corn oil (RESKU). The mentioned vegetable oils and mixtures were heated at the temperatures of 165 , 185, 200 and 220 °C, over the periods of 10, 30 and 60 minutes in a deep fryer. To assess the oxidative stability of the vegetable oil samples, an analysis was carried out to define a peroxide and anisidine value (number), free fatty acids as well as the composition of fatty acids before and after heating, at each set temperature and time of exposure. All the samples showed lesser oxidative stability with the increasing of temperature and time of heating. However, the most stable was extra virgin olive oil (EDMU). Omega-3 and trans fatty acids did not show statistically significant changes during heating.

**KVALITETA MASLINOVOG ULJA DOBIVENOG OD
SORTE OBLICA SA PODRUČJA BOSNE I
HERCEGOVINE
THE QUALITY OF VIRGIN OLIVE OIL OBTAINED OF
OBLICA VARIETY FROM THE BOSNIA AND
HERZEGOVINA**

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Considering its numerous nutritive values, the olive represents the basis of the so-called Mediterranean nutrition, which has often been identified with the term 'healthy nutrition'. Consumers increasingly understand the importance of olive oil quality and stability as well as the nutritional benefits of monosaturated oil with naturally low levels of saturated fatty acids. Oblica is the most common olive variety in Bosnia and Herzegovina. The fatty acid profile is important in determining olive oil quality and stability. In this research the samples of extra virgin olive oil, from two regions of Bosnia and Herzegovina: Neum and Ljubuski region were analyzed by determination of fatty acids composition, peroxide index and free fatty acids content.

There was no statistically significant difference in the air temperature and precipitation between investigated areas. Mean values of air temperature in Ljubuski region was 1.86 % higher in comparison with Neum region, while precipitation in Neum region was 5.45 % higher than in Ljubuski region. There was not statistically significant difference in fatty acid, peroxide index and free fatty acids content between the samples of extra virgin olive oil from both different region ($p < 0.05$).

Key words: Oblica, oil, fatty acid, stability

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FUNKCIONALNA SVOJSTVA NEKIH VRSTA GOMOLJASTOG POVRĆA FUNCTIONAL PROPERTIES OF SOME TUBER TYPES

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Krumpir (*Solanum tuberosum* L.) i batat ili slatki krumpir (*Ipomoea batatas*) gomoljaste su biljke iz reda *Solanales*, odlikuju se visokom energetsom i nutritivnom vrijednošću. Pojedine vrste krumpira i batata sadrže značajne količine polifenola koji su uslijed snažnog antioksidacijskog djelovanja poznati po svojim pozitivnim učincima na zdravlje ljudi. S obzirom na visoku zastupljenost krumpira u prehrani ljudi, ova se namirnica smatra trećim najvažnijim prehrambenim izvorom polifenola. U posljednje vrijeme postoji veliki interes za „obojene“ sorte krumpira, uključujući plavi i crveni krumpir. Spojevi odgovorni za plavu i crvenu boju mesa krumpira su antocijanini – polifenolni spojevi koji se ubrajaju među najjače prirodne antioksidanse. U ovom radu određivan je antioksidacijski kapacitet, te sadržaj ukupnih polifenola i ukupnih antocijanina u različitim vrstama gomoljastog povrća iz reda *Solanales*. Analizirani su krumpiri bijelog, plavog i crvenog mesa, te batat bijele i narančaste boje mesa. Ekstrakcija polifenola provedena je primjenom ultrazvučnih valova uz otapalo metanol/HCl = 99/1, v/v. Za određivanje sadržaja ukupnih polifenola korištena je spektrofotometrijska Folin-Ciocalteu (FC) metoda. Galna kiselina korištena je kao standard te je sadržaj ukupnih polifenola izražen u ekvivalentima galne kiseline (mg GAE / 100 g svježe mase povrća). Najveći sadržaj ukupnih polifenola određen je u plavom (92,69 mg GAE / 100 g FW), dok bijeli krumpir sadrži najmanji udio (30,34 GAE / 100 g FW). U bijelom i narančastom batatu iznosio je 79,49 GAE / 100 g FW odnosno 72,33 GAE / 100 g FW. Sadržaj ukupnih antocijanina određen je pH-diferencijalnom metodom i izražen u ekvivalentima cijanidin-3-glukozida. Antocijanini su nađeni jedino u plavom i crvenom krumpiru, u količini od 26,57 odnosno 6,77 mg Cyd-3-glu / 100 g FW. Antioksidacijski kapacitet ekstrakata analiziranog povrća određen je DPPH metodom i izražen u ekvivalentima Troloxa (TE) / kg svježe mase povrća. Iznenadujuće, najveći antioksidacijski kapacitet određen je za narančasti batat (8,43 mmol TE / kg FW), a najniži za plavi krumpir (6,73 mmol TE / kg FW). Očekivana korelacija između sadržaja ukupnih polifenola i antioksidacijske aktivnosti nije dobivena, vjerojatno zbog toga što ukupnom antioksidacijskom kapacitetu doprinose i ne-fenolni antioksidansi, koji su u analiziranom povrću prisutni u značajnim količinama.

**UTJECAJ ANTIOKSIDANSA NA OKSIDACIJSKU
STABILNOST SMJESE SEZAMOVOG ULJA
I BILJNOG ULJA
INFLUENCE OF ANTIOXIDANTS ON THE OXIDATIVE
STABILITY OF THE MIXTURE OF SESAME OIL AND
VEGETABLE OIL**

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One of the major problems during production, application and processing of edible oils is oxidation of lipids, which results in significant change of chemical, sensory and nutritional properties. In this paper, the influence of synthetic antioxidants propyl gallate (0.01 %) and natural antioxidant: extracts of rosemary OxyLess.CS (0.1 %) and green tea extract (0.1 %), on the oxidative stability of sesame oil mixtures and other types of vegetable oil (50:50) was monitored. To test the stability of oxidation the following types of vegetable oils were used: sesame oil, peanut oil, walnut oil, almond oil, rapeseed oil, extra virgin olive oil. Oxidative stability of oil mixtures and the effect of antioxidants were determined by Schaal oven test (63 °C). The extent of oil oxidation was expressed as peroxide value during 4 days of test. Compared to pure vegetable oils, mixtures of oils with sesame oil were less prone to oxidation. Natural antioxidant OxyLess.CS rosemary extracts and green tea extract effectively protects the oil mixture from oxidative deterioration as compared to the addition of synthetic antioxidants propyl gallate.

Key words: vegetable oil, oxidative stability, rosemary extract, green tea extract, propyl gallate

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UTJECAJ PROCESNIH PARAMETARA NA REOLOŠKA SVOJSTVA SALATNE MAJONEZE INFLUENCE OF PROCESS PARAMETERS ON THE RHEOLOGICAL PROPERTIES OF SALAD MAYONNAISE

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U ovom radu istraživana su reološka svojstva salatne majoneze. Istraživan je utjecaj procesnih parametara brzine rotacije rotora homogenizatora i vrijeme trajanja pripreme majoneze na reološka svojstva. Mehanički proces homogenizacije emulzije proveden je kod 10 000, 12 000 i 15 000 o/min pri sobnoj temperaturi. Majoneza sadrži 65 % ulja (hladno prešano suncokretovo ulje), žumanjak jajeta, glukozu, mlijeko u prahu, proteine graška, ocat, sol, senf, vinsku kiselinu i destiliranu vodu. Mjerenja reoloških svojstava provedena su na rotacijskom viskozimetru sa koncentričnim cilindrima pri temperaturama 10 °C i 25 °C. Iz dobivenih podataka izračunati su reološki parametri koeficijent konzistencije, indeks tečenja i prividna viskoznost. Rezultati istraživanja pokazali su da brzina rotacije rotora homogenizatora i vrijeme trajanja procesa pripreme majoneze utječu na reološka svojstva. Homogenizacija kod brzine rotora 12000 o/min rezultira većim vrijednostima konzistencije i prividne viskoznosti majoneze. Priprema majoneze kod 15000 o/min dovodi do smanjenja navedenih reoloških parametara.

Ključne riječi: majoneza, reološka svojstva, procesni parametri

INTAKE OF TANNIC ACID FROM TEA AND COFFEE AS A RISK FACTOR FOR IRON BIOAVAILABILITY IN PREGNANT WOMEN

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Iron binding polyphenols are widespread in foods because they occur naturally in a variety of cereals, vegetables, and spices, and in many beverages such as wine, coffee, and tea. These beverages strongly inhibit the absorption of nonheme iron; a cup of tea (cca 200 ml) reduces iron absorption by 75–80 % and a cup of coffee (cca 150 ml) up to 60 %. Pregnancy presents a critical period for both woman and a child, and iron blood status of a pregnant woman is especially important since iron deficiency and anaemia, which are the most common deficiencies among pregnant women, have adverse impact on pregnancy outcomes. Therefore, the aim was to determine the intake of tea and coffee, and intake of iron binding polyphenols from these beverages (expressed as tannic acid equivalents) in pregnant women. A consumption of tea and coffee was noted in a population of pregnant women (N = 222) during the 1st, 2nd and the 3rd trimester. Total of 153 pregnant women (68.9 %) were drinking either coffee, tea or both during pregnancy. Tea was consumed by 18.0 % (n= 40) of pregnant women, ranging from 250 ml up to 540 ml per day. Mostly preferred were different fruit teas (such as blueberry, forest fruits), dog-rose, camomile and mint tea. Coffee was consumed in much higher percentage, by 58.6 % (n = 130) of pregnant women, ranging from 100 ml up to even 600 ml per day, preferably as instant coffee. 13 women simultaneously drank coffee and tea, while 4 women combined drinking tea or coffee during particular trimester. Total intake of tannic acid equivalents from tea and coffee was the highest in the 2nd trimester (median of 15.0 mg/day), while for the 1st and the 3rd trimester median was 11.0 mg/day. This is in compliance with the findings that physiologic changes during pregnancy (nausea in the 1st and heart-burn in the 3rd trimester) lead to avoidance of consumption in a particular trimester. During the 1st trimester 20 coffee drinkers and 7 tea drinkers gave up their preferred beverage due to nausea. At the 3rd trimester 20 out of 113 pregnant women who drank only coffee (17.7 %) and 6 out of 23 who drank only tea (26.1 %) stopped drinking a particular beverage, referring heart-burn as a reason. In conclusion, even though for some pregnant women physiology of pregnancy leads to lowering consumption or absolute avoiding of preferred beverage, coffee and tea are highly consumed among pregnant women and can be considered as an important factor for low iron bioavailability.

Key words: tannic acid, tea, coffee, pregnant women

FATTY ACID AND TRIACYLGLYCEROL PROFILE OF LEVANTINKA VIRGIN OLIVE OIL

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The scientific work on the authenticity and quality of olive oil is an ever-growing area. In the last decade great attention has been focused on characterization of monovarietal virgin olive oils in order to protect and preserve olive biodiversity in major olive growing countries, as well as in Croatia. Virgin olive oil (VOOs) contains about 98 % neutral lipids, mainly triglycerides (96-97 %), a small quantity of diglycerides (1-2 %) and a variable quantity of free fatty acids, which are used as a marker of oil quality. The object of this study is to explore the possibilities of different chemical parameters, normally determined in olive oil analysis, to differentiate and classify olive oil samples of different origin, in order to confirm the authenticity of Levantinka VOOs, one of the most common autochthonous olive variety in the Dalmatia region. The paper describes characteristics of virgin olive oils coming from three different geographic origins, i.e. Kaštela, island Korčula and island Brač. Main chemical quality parameters were evaluated (free fatty acids, peroxide value and UV-spectrophotometric oxidation indexes (k232 and k270), as well as analyses of fatty acid and triglyceride composition, as one of authenticity parameters of olive oil were also evaluated according to international analytical methods. Some of the most important relationships of fatty acids in olive oil are described, by which it essentially differs from other vegetable oils (proportion of oleic, linoleic and linolenic acid).

Key words: authenticity, fatty acids, quality, triglycerides, virgin olive oil

FUSARIUM MYCOTOXINS

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Mycotoxins are group of toxic secondary metabolites produced by fungi when they undergo stressful conditions. Fungi from genus *Fusarium* are widely spread in Europe and Croatia. A significant fungus for Croatia is *Fusarium graminearum* because of the optimal agro-climatic conditions (warmer temperatures and high humidity) in which it can produce mycotoxins deoxynivalenol, nivalenol, T-2, HT-2, diacetoxyscirpenol and zearalenone. Fungi from genus *Fusarium* produce over 400 secondary metabolites and only deoxynivalenol (carcinogen), T-2 and HT-2 (haematotoxic), zearalenone (endocrine disruptor) and fumonisins (cytotoxic) are regulated by regulations on maximally allowed content of certain food contaminants in food (NN 154/08; EC 401/2006). By regulations on undesirable and forbidden substances in animal feed (NN 118/07) following *Fusarium* mycotoxins are regulated: deoxynivalenol, zearalenone, fumonisins T-2 and HT-2 toxins. Other relevant *Fusarium* mycotoxins that are not regulated by these regulations are nivalenol, 3-diacetoxynivalenol, 15-diacetoxynivalenol, fusarenon X and diacetoxyscirpenol. EFSA (European Food Safety Authority) requested some additional researches for the following *Fusarium* mycotoxins: enniatins (*F. miniliforme*, *F. avanceum*, *F. nivale*), moniliformin (*F. moniliforme*, *F. nivale*, *F. culmorum*), and diacetoxyscirpenol (*F. moniliforme*, *F. equiseti*). Regulated *Fusarium* mycotoxins can be found in: cereals and their products, baby food, milk, meat, wine, grapes, fruit and fruit products, beer, cocoa beans, coffee, spices and animal feed.

Key words: fungi, mycotoxins, *Fusarium*;

MYCOTOXIN DETECTION METHODS AND LEGISLATION

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Mycotoxins are group of toxic secondary metabolites produced by moulds and there is more than 400 different mycotoxins known. They can be found in food as a result of fungal infestation of crops, directly eaten by humans or used as a livestock feed. Due to their toxicity, there were established regulatory limits. From all mycotoxins there are only 13 regulated in Croatia and EU: Aflatoxin B1, B2, G1, G2, M1, Ochratoxin A, Patulin, Deoxynivalenol, Zearalenone, Fumonisin B1, Fumonisin B2, T-2 toxin and HT-2 toxin (last two have only analytical requirements, not maximum tolerable concentration). European Food Safety Agency (EFSA) has asked for additional attention for following mycotoxins: Enniatines, Beauvericin, Alternaria toxins, Citrinin, Sterigmatocystine, Moniliformin, Fumonisin, Diacetoxyscirpenol and Phomopsis. In legislation analytical criteria that laboratories for quantification of mycotoxins have to meet are defined (NN 45/08; EC 401/2006). Special attention is given to recovery, repeatability, reproducibility and LOD /LOQ. Some older methods cannot meet all criteria, due to some lacks such as low sensitivity, specificity, selectivity and accuracy, while new methods which are using LC-MS/MS techniques can easier meet performance and the results are more reliable due to determining masses of particles, their fragments and quantifier/qualifier ratio.

Key words: mycotoxins, detection methods, legislation

**UČINCI KEMIJSKE INTERESTERIFIKACIJE NA
FIZIKALNO KEMIJSKA SVOJSTVA BINARNIH SMJESA
PALMINOG STEARINA SA KOKOSOVIM, REPIČINIM I
SOJINIM ULJEM
EFFECTS OF CHEMICAL INTERESTERIFICATION ON
PHYSICOCHEMICAL PROPERTIES OF BINARY
MIXTURES OF PAML STEARIN WITH COCONUT,
RAPESEED AND SOYBEAN OIL**

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Interesterifikacijom biljnih masti i tekućih ulja moguće je dobiti masnu sirovinu bez trans izomera, pogodnu za proizvodnju tvrdih i mazivih margarina, te masti za industrijsku primjenu. Na poluindustrijskom postrojenju proučavani su neki važniji parametri pri postupku kemijske interesterifikacije binarnih smjesa masti i ulja s natrij metoksidom kao katalizatorom. Proučavane smjese su: palmin stearin/kokosovo ulje u omjeru 60:40 (PS/CO 60/40), palmin stearin/kokosovo ulje u omjeru 80:20 (PS/CO 80/20), palmin stearin/repičino ulje u omjeru 85:15 (PS/RO 85/15) i palmin stearin/sojino ulje u omjeru 85:15 (PS/SO 85/15). Navedene smjese interesterificirane su pri temperaturama 70 °C i 90 °C sa 0,2 % i 0,4 % katalizatora kroz vrijeme od 30 i 60 minuta. Izvorne i interesterificirane smjese analizirane su kroz sastav masnih kiselina i sadržaj trans izomera, točku tališta, sadržaj čvrstih triglicerida (SFC), vlage, sapuna, slobodnih masnih kiselina i peroksidni broj. Količina katalizatora pokazala se kao statistički značajan parametar za sadržaj čvrstih triglicerida i točku tališta interesterificiranih smjesa. Optimalni parametri u ovom pokusu bili su 30 minuta pri 70 °C i 0,4 % katalizatora. Prema fizikalno kemijskim svojstvima sve interesterificirane smjese imaju potencijal kao moguća sirovina za izradu margarina i masti, a kao najpogodnija pokazala se smjesa (PS/SO 85/15).

**UTJECAJ PASTERIZACIJE I DODATKA
HIDROKOLOIDA NA REOLOŠKA SVOJSTVA
KAŠE MALINE
INFLUENCE OF PASTEURIZATION AND
HYDROCOLLOIDS ADDITION ON RHEOLOGICAL
PROPERTIES OF RASPBERRY PUREE**

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Hydrocolloids are used as an additive in many foods to provide better rheological properties and for gelling. Natural starch is not suitable for application in many food products because of retrogradation, syneresis and low stability. In order to obtain the required functional properties, instead native starch we often use hydrocolloids or modified starches. This paper deals with the influence of pasteurization and addition of hydrocolloids on rheological properties of raspberry puree. Raspberry purees were prepared with addition of hydrocolloids, karaya (0.05 %) or guar (0.05 %). The rheological properties (shear stress and shear rate at different temperatures) were measured by rotational viscometer, model DV – III + Digital Rheometer, Brookfield Engineering Laboratories. Consistency coefficient k and flow index n were calculated from measured data (τ and D). Results showed that guar gum addition in raspberry purees had higher impact on puree consistency than gum karaya. All raspberry purees were Non-Newtonian stationary fluids at measured temperatures. Pasteurization also had influence on rheological properties of puree with addition of hydrocolloids, but had no effect on above mentioned properties of basic raspberry puree.

Keywords: Raspberry purees, pasteurization, rheological properties, hydrocolloids

**PRIMJENA MULTIVARIJANTNE ANALIZE KAO
METODE ZA KLASIFIKACIJU KUPINOVOG VINA NA
TEMELJU UZGOJA PLODA
APPLICATION OF MULTIVARIATE ANALYSIS FOR THE
CLASSIFICATION OF CROATIAN BLACKBERRY WINES
ACCORDING TO GROWING FRUIT**

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Principal component analysis (PCA), linear discriminant analysis (LDA) and other multivariate statistical methods have been widely applied for wine classification using different variables such as contents of minerals, trace elements, amino acids, phenolic compounds. In this study 90 analyzed parameters (nutritional, biologically active and toxic components, physicochemical parameters and antioxidant activity) were determined in fifteen samples of Croatian blackberry wines. PCA and LDA were carried out using the original data set with the standard procedure (using all variables). Also, principal components (PCs) derived from the original data set with the eigenvalues >1.0 were used for further LDA analysis. Results of PCA analysis conducted on blackberry wine from conventionally and organically grown fruit separated 14 PCs from all analyzed parameters (the original set of variables) which completely explain the variability of blackberry wine. LDA analysis separated 7 PCs which statistically extremely separate two investigated groups (sensitivity and specificity of 100 %) along with exact prediction of the distribution to 100 %. It was also obtained from the results of the LDA analysis carried out on the original group data which separated 12 components of blackberry wine that can be used to classify blackberry wines into organic or conventional groups.

Keywords: blackberry wine, conventionally or organically grown, PCA, LDA

**PROMJENE SADRŽAJA SO₂ U CRNOM VINU TIJEKOM
ČUVANJA U RAZLIČITOJ AMBALAŽI
CONTENT CHANGES OF SO₂ IN RED WINE DURING
STORAGE IN DIFFERENT PACKAGING**

Nebojša Kojić

Vupik d.d., Vukovar, Hrvatska

U radu će biti istraživani utjecaji različitih ambalaža za vino na koncentracije slobodnog i ukupnog sumpor dioksida sorte Vranac, Gevgelijsko-valandovsko vinogorje, R Makedonija. Istraživano vino bit će punjeno u sljedeću ambalažu: litrena staklena boca sa krunskim zatvaračem, staklena boca volumena 0,75 l sa plutenim čepom (butelja), plastična boca volumena 5 l sa navojnim zatvaračem, vitop vrećice od Al-folije volumena 3 l, kartonska ambalaža u obliku bricka volumena 1 l. Analiza slobodnog i ukupnog sumpora provesti će se metodom po Ripperu i to tijekom dva i pol mjeseca skladištenja na temperaturama sličnim onima u trgovini. Za očekivati je da će se koncentracije SO₂ najbrže smanjiti u vinu punjenom u plastičnu ambalažu obzirom na karakteristike plastike, a koje će biti predočene u cjelovitom tekstu nakon dva i pol mjeseca skladištenja vina.

Ključne riječi: slobodni sumpor dioksid, ukupni sumpor dioksid, ambalaža, crno vino.

MEDICINSKA BIOKEMIJA I FARMACIJA
MEDICAL BIOCHEMISTRY AND PHARMACY

***IN VITRO* ANTITUMOR EFFECT OF DOMESTIC *APIS MELLIFERA* BEE VENOM AND MELITTIN**

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Bee venom therapy has been used as a traditional medicine to treat a variety of illness, such as arthritis, rheumatism, back pain, tumours, and skin diseases. To test antitumor potential of domestic *Apis mellifera* bee venom (BV) we used selected cell lines, tumour colon adenocarcinoma (CaCo-2), cervix adenocarcinoma (HeLa), Burkitt lymphoma (RAJI), chronic myeloid leukaemia in blasted crisis (K562) of human origin and Madine-Darby canine kidney (MDCK) cells. Final concentration range of BV was 0.001 to 1 mg/mL. As a standard compound was used melittin in a concentration range of 0.001 to 0.1 mg/mL. The cytotoxic effect of BV and melittin were evaluated after 72 hours of incubation by the MTT assay. Obtained results showed that leukaemia cells were more sensitive to BV and melittin. The 50 % survival of treated tumor adherent cell (IC₅₀) was achieved by application of 0.1 mg/mL of BV and melittin. As expected, the most resistant to BV and melittin was normal MDCK cells. BV as a natural remedy, through the activity of lytic peptides mellitin, can be useful as a new targeted therapy in anticancer treatment.

DRY EXTRACTS OF *SATUREJA MONTANA*, BENEFITIAL COMPOUNDS, PROPERTIES AND POSSIBLE APPLICATIONS

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Many reports have been published on the antioxidant activity of bioactive plant extracts. These reports have been initiated by an increasing consumer demands for safe and natural food products/additives. Beside consumer's interest in food safe products, interest in plant extracts as a sources of important bioactive compounds that could be used in many diseases prevention is exponentially growing. As a source of bioactive compounds, primarily antioxidants, Winter savory or *Satureja Montana* L, of Serbian origin, has been investigated. The genus *Satureja montana* L. belongs to the *Lamiaceae* family, and comprises around 30 species. In this study two *S. montana* dry extracts were prepared and analyzed. First extract was prepared from liquid extract by spray drying process, with input temperature around 120 °C and output temperature around 75 °C. Second dry extract was prepared by the process of freeze-drying: liquid *S. montana* extract was frozen to the temperature of – 20 °C; temperature in condenser during sublimation process was around -50 °C, while pressure in the chamber was 0.001 mbar; during the desorption process maximal temperature in the chamber was 30 °C; total drying time was 36 hours. In prepared extracts content of antioxidant compounds (total phenols and total flavonoids) has been determine. To define the antioxidant activity of investigated extracts DPPH test was performed. This way analyzed extracts were combined, in amount of 2.5 %, in mixture with starch, lactose and Aerosil®, while combination of water soluble starch and corn starch was added as a components binder. Obtained mixture was used for preparation of tablets with average weight around 250 mg.

Key words: *Satureja montana*, freeze-drying, spray drying, antioxidants, tablets

This work was financial supported by the Serbian Ministry of Education and Science, Project No. TR 31013.

EKSTRAKTI NATIVNIH I AUTOFERMENTISANIH JEZIČASTIH CVETOVA KAMILICE DOBIJENI RAZLIČITIM METODAMA EKSTRAKCIJE EXTRACTS OF NATIVE AND AUTOFERMENTED CHAMOMILE LIGULATE FLOWERS OBTAINED BY DIFFERENT EXTRACTION METHODS

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Chamomile (*Matricaria chamomilla* L.) is one of the most widely used and well know medicinal plant in the world. The flowers of chamomile contain flavonoids, coumarine, malic acid, proteins, sugars, lipids and mineral elements. The aim of this study was to compare different extraction methods of native chamomile ligulate flowers (CLF) and autofermented chamomile ligulate flowers (A-CLF). Three different extraction methods (Soxhlet extraction, maceration and percolation) were applied. In all methods same solvent (70 % ethanol) was used. The extraction yield, total phenols content and total flavonoids content were determined in obtained extracts (Table 1). The highest extraction yield, as well as total phenols and flavonoids content, in CLF case, were obtained by Soxhlet extraction methods. Same can be observed in A-CLF case. Antioxidant activities of extracts were tested using a standard DPPH procedure. According to the results of IC₅₀ values, the best antioxidant activity possess CLF and A-CLF extracts obtained by 70 % ethanol using Soxhlet as the extraction procedure too. Research was conducted with support from the Ministry of Education and Science Republic of Serbia within the project TR31013.

Table 1. Extraction yield, total phenols content (TP), total flavonoids content (TF) and IC₅₀ values of investigation samples

Method	Sample	Extraction yield (%, w/w)	TP (mg CAE/g [*])	TF (mg RE/g [*])	IC ₅₀ (mg [*] /ml)
Percolation	CLF	18.49	14.52	4.85	0.111
	A-CLF	16.73	15.59	4.68	0.196
Maceration	CLF	32.16	38.35	20.28	0.086
	A-CLF	34.35	61.54	22.43	0.144
Soxhlet	CLF	32.62	57.18	41.44	0.055
	A-CLF	44.93	9.5	35.75	0.057

* drugs

Keywords: Chamomila, Extraction, antioxidant compounds, DPPH.

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**SUHI EKSTRAKTI RTANJSKOG ČAJA (*SATUREJA MONTANA* L.), ZNAČAJNE KOMPONENTE I OSOBINE
TE NJIHOVA POTENCIJALNA UPOTREBA
DRY EXTRACTS OF *SATUREJA MONTANA*, THEIR
BENEFITIAL COMPOUNDS AND PROPERTIES, AND
POSSIBLE APPLICATIONS**

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Many reports have been published on the antioxidant activity of bioactive plant extracts. These reports have been initiated by an increasing consumer demands for safe and natural food products/additives. Beside consumers' interest in food safe products, interest in plant extracts as a sources of important bioactive compounds that could be used in many diseases prevention is exponentially growing. As a source of bioactive compounds, primarily antioxidants, Winter savory or *Satureja Montana* L, of Serbian origin, has been investigated. The genus *Satureja montana* L. belongs to the *Lamiaceae* family, and comprises around 30 species. In this study two *S. montana* dry extracts were prepared and analyzed. First extract was prepared by spray drying process, with input temperature around 120 °C and output temperature around 75 °C. Second extract was prepared by the process of freeze-drying: liquid *S. montana* extract was frozen to the temperature of - 20 °C; temperature in condenser during sublimation process was around - 50 °C, while pressure in the chamber was 0.001 mbar; during the desorption process maximal temperature in the chamber was 30 °C; total drying time was 36 hours.

In prepared extracts content of antioxidant compounds (total phenols and total flavonoids) has been determine. To define the antioxidant activity of investigated extracts DPPH test was performed. This way analyzed extracts were combined, in amount of 2.5 %, in mixture with strach, lactose and aerosil, while combination of water soluble starch and corn starch was added as a components binder. Obtained mixture was used for preparation of tablets with average weight around 250 mg.

Key words: *Satureja montana*, freeze-drying, spray drying, antioxidants, tablets

KEMIJA U POLJOPRIVREDI I ŠUMARSTVU
CHEMISTRY IN AGRICULTURE AND FORESTRY

**UTJECAJ GNOJIDBE SINTETSKIM ZEOLITIMA NA
MINERALNI SASTAV LUPINE (*LUPINUS ALBUS* L.)
THE INFLUENCE OF SYNTHETIC ZEOLITES
FERTILIZATION ON WHITE LUPINE
(*LUPINUS ALBUS* L.) MINERAL COMPOSITION**

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Reakcija tla najvažniji je čimbenik koji regulira primanje biogenih elemenata, a time i pojavu deficijencija. U alkalnim, karbonatnim tlima, deficijencije cinka i mangana su česte upravo zahvaljujući činjenici da se formiraju teško topivi spojevi koji značajno smanjuju njihovu dostupnost biljkama. Upotreba zeolita kao gnojiva temelji se na činjenici da su zamjenjivi kationi u zeolitu sporo otpuštajući izvor hranjiva koji bi trebao osigurati stabilnu i konstantnu opskrbu biljkama kroz nekoliko vegetacijskih godina, unatoč negativnim kemijskim osobinama tla. Cilj ovog istraživanja bio je stoga utvrditi utjecaj gnojidbe modificiranim sintetskim zeolitima, putem tla, na mineralni sastav nadzemnog dijela lupine *Lupinus albus* L. U tu svrhu provedeno je u vegetacijskoj komori, tijekom 52 dana, istraživanje na alkalnom tlu (pH KCl = 7.4). Gnojidba Zn i Mn obavljena je u obliku sintetskog Zeolita A u kojem su ionskom zamjenom Na ioni zamijenjeni kationima Zn, Mn. Istraživanje je provedeno po slučajnom bločnom rasporedu s 4 gnojidbena tretmana (Kontrola, NPK, Zeoliti mix, NPK + Zeoliti mix). Temeljem rezultata istraživanja vidljivo je da je pri tretmanu Zeoliti mix utvrđena statistički značajno veća količina Mn u nadzemnim dijelovima lupine u odnosu na sve ostale gnojidbene tretmane dok se količina Zn nije statistički razlikovala neovisno o gnojidbenim tretmanima.

Ključne riječi: Zeolit A, Cink (Zn), Mangan (Mn), lupina

ODREĐIVANJE RASPOLOŽIVOSTI CD I ZN POMOĆU REGRESIJSKIH MODELA USE OF REGRESSION MODELS IN PREDICTION OF CD AND ZN GRAIN CONCENTRATIONS

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Strong and mild acids are usually poor indicators of trace metal availability. Present study investigated the relationship between several extraction methods (strong - *aqua regia* and ultra pure HNO₃, mild - EDTA and weak - deionised water) and their ability to predict grain concentrations of Cd and Zn. Since the extraction of trace metals by deionised water was not analytically determined at the sites where wheat grain samples were collected, the information on water extraction, i.e. soil solution concentration, was predicted by regression models. In soils with low concentrations, soil properties seem to play an important role in solubility and availability of trace metals such as Cd and Zn. Our hypothesis was that grain trace metal concentrations will show better correlation with weak extractant such as water (even when information on water extraction is obtained by regression modelling) than strong or mild acid such as *aqua regia* and EDTA. The results confirmed our hypothesis showing no correlation between grain concentrations and soil concentrations of Zn and Cd extracted by *aqua regia* and EDTA. However, regression modelling predicting soil solution concentrations and free ion activity (FIA) showed good correlation between predicted values of water extractable fraction and grain concentrations of Zn and Cd.

Keywords: Extraction methods, Plant availability, Soil solution, Trace metals

UTJECAJ NEUTRALIZACIJE KISELOSTI TLA NA PRISTUPAČNOST FOSFORA EFFECTS OF SOIL ACIDITY NEUTRALIZATION ON PHOSPHORUS BIOAVAILABILITY

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Soil acidification results with significant soil chemical changes, especially with availability changes of certain macro and microelements, as well as potentially toxic elements. The aim of this paper was to determine influence of excessive soil acidity neutralization to phosphorus availability change. Liming and fertilization experiment was set up in 20 L volume plastic pots with two types of acid soils with different texture from Donji Miholjac (DM) and Magadenovac (MA) locality in a year 2004. and 2005. In order to neutralize excessive soil acidity, ten liming and fertilization treatments were applied in four repetitions. Liming doses were 7.5 and 15 t/ha of mischkalk (65 % CaO) with calcium carbonate equivalent (CCE) 116.04 %, and effective neutralizing value (ENV) 82.56 %. Organic fertilizer doses were 20 and 40 t/ha. Alfalfa cultivar Osječka 66 was sown as indicator plant. Soil was sampled and analysed after first and second year of investigation and plant material was sampled in three cuttings in each year and analysed. Results showed significant increase of soil pH values influenced by liming treatments. Soil acidity neutralization resulted with increment of AL-available soil phosphorus on average 1.8 – 4.9 mg/kg P₂O₅ per t of applied CaCO₃, where phosphorus availability increment per unit of applied liming material was higher for lower liming doses applied and in soils with higher initial level of phosphorus availability. Organic fertilization resulted with phosphorus availability increment of 7.3 – 10.2 mg/kg P₂O₅ per every 10 t of applied organic fertilizer. Increment of liming rate and organic fertilizer rate showed phosphorus concentration increase in alfalfa leaf and stalk.

Key words: soil acidity, liming, organic fertilization, phosphorus availability

RASPODJELA TEKUĆINE S POLJOPRIVREDNIM MLAZNICAMA LECHLER OC3 SPRAY DISTRIBUTION WITH AGRICULTURAL NOZZLES LECHLER OC3

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U novijoj, intenzivnoj poljoprivredi, sve se više vodi računa o održivom razvoju i zaštiti okoliša. Primjeri iz EU pokazuju nam kako je intenzivan razvoj i proizvodnja narušila sklad s prirodom pa su se počele uvoditi mjere i posebni zakoni kako isti ne bi uzeo maha. Novim zakonima u Republici Hrvatskoj kao i EU, posebice bi se utjecalo na tehničke sustave u zaštiti bilja i njihovim obaveznim testiranjima kako bi aplikacija pesticida bila opravdana i ispravna. Jedan od važnih čimbenika aplikacije pesticida je njihovo ujednačeno i kvalitetno nanošenje na cilj zaštite bilja. Stoga, svaka poljoprivredna mlaznica mora ostvariti standarde optimalne raspodjele tekućine. U radu su prikazani rezultati istraživanja površinske i volumne raspodjele tekućine te protoka mlaznice pri radu Lechler OC3 mlaznice. Istraživanja su obavljena pri radnom tlaku 2, 3 i 4 bara, te pri radnoj visini od 40, 50 i 60 cm.

Ključne riječi: poljoprivredna mlaznica, protok mlaznice, raspodjela tekućine, visina prskanja, radni tlak

ZAŠTITA OKOLIŠA
ENVIRONMENTAL PROTECTION

**PRIMJENA LIHENOLOŠKIH ISTRAŽIVANJA
U PROCJENI KAKVOĆE ZRAKA NA PODRUČJU GRADA
SLATINE (SLAVONIJA, HRVATSKA)
APPLICATION OF LICHENOLOGICAL SURVEY FOR
AIR QUALITY ASSESSMENT IN THE AREA OF CITY OF
SLATINA (SLAVONIA REGION, CROATIA)**

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It is known that lichens, due to their sensitivity to presence of atmospheric pollutants, are used as bioindicators for air quality assessment in a particular area. Lichen flora in the wider area of the City of Slatina was surveyed by repeated field visits in 2011 and 2012. Slatina is a city in Slavonia region, located in Virovitica-Podravina County, at the contact of the Drava River valley and the foothills of Papuk. Four localities were chosen which are distinctive in geographical position, distribution of habitat types and intensity of anthropogenic impact. Lichen specimens were collected from the soil, concrete substrate, trees and shrubs at height up to 2 m above ground. A total of 49 species and 1 subspecies, classified into 31 genera of lichenized fungi, have been recorded. Crustose lichens dominate (56 %), followed by foliose (36 %) and fruticose (8 %) forms. Regarding the substrate preference, 45 lichen species were found epiphytic on bark of 18 species of woody plants in total. According to the analyses of lichen flora composition and distribution of lichen species, weak to very weak air pollution level was determined. Lichen diversity is expectedly poorer in the urbanized area and in the proximity of factory facilities. More favourable environmental conditions are present in the woodland areas outside the settlements, where the richer lichen flora was observed. Finding of endangered species *Lobaria pulmonaria* on the bark of pedunculate oaks, which is an indicator of undisturbed forest ecosystems, is of outstanding importance.

**MOGUĆI RAZVOJ GOSPODARENJA OTPADOM GRADA
ZAGREBA NA TEMELJU BILANCE KOLIČINA I
SASTAVA OTPADA
POSSIBLE DEVELOPMENT OF WASTE MANAGEMENT
IN THE CITY OF ZAGREB BASED ON BALANCE OF
WASTE AND WASTE COMPOSITION**

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Jedan od ciljeva zaštite okoliša je sprječavanje i smanjenje onečišćenja okoliša, između ostalog i otpadom. Nadzor nad tokovima otpadom u Gradu Zagrebu provodi se i izradom bilanci otpada te periodičnim provjerama sastava komunalnog otpada iz kućanstava. Na temelju analiza količina i sastava otpada moguće je odrediti mogući razvoj gospodarenja otpadom na području Grada Zagreba koji se temelji na reciklaži dijela nastalog otpada i energetske uporabi ostatnog otpada. Stoga se ovim radom analiziraju postojeći podaci i iznose procjene karakteristika budućih tokova otpada za obradu u skladu s važećim strateškim i planskim dokumentima iz područja gospodarenja otpadom. Postojeća saznanja o miješanom komunalnom otpadu pokazuju da otprilike 1/3 otpada predstavlja ambalažni otpad reguliran posebnim pravilnikom, zatim 1/3 biorazgradivi otpad čiji je trend smanjenja količina za odlaganje propisan nacionalnom strategijom gospodarenja otpadom te 1/3 se odnosi na gorivi otpad pogodan za energetske uporabu. Na temelju mogućeg razvoja udjela pojedinih komponenti, pretpostavlja se porast udjela ambalažnog otpada na oko 65 %, smanjenje udjela gorivog otpada na oko 25 % te pad udjela biorazgradivog otpada na oko 10 %. Dobiveni rezultati su u skladu s iskustvima razvijenih zemalja te opredjeljenjem Grada Zagreba glede gospodarenja otpadom.

Ključne riječi: gospodarenje otpadom, bilanca otpada, sastav komunalnog otpada

**BIOLOŠKA OBRADA PROCJEDNE VODE NASTALE IZ
OTPADNOG DUHANSKOG PRAHA:
EKSPERIMENTI I KINETIČKA ANALIZA
BIOLOGICAL TREATMENT OF LEACHATE
GENERATED FROM TOBACCO DUST WASTE:
EXPERIMENTS AND KINETIC ANALYSIS**

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Landfill leachate is defined as the aqueous effluent generated as a consequence of rainwater percolation through wastes, biochemical processes in waste's cells and the inherent water content of wastes themselves. Biological treatments are often used for the removal of the bulk of leachate with high chemical oxygen demand (COD) values primarily due to their higher reliability, simplicity and cost effectiveness of these processes.

The aim of this work was to study the efficiency of biodegradation of organic pollutants in laboratory prepared leachate from tobacco dust waste under batch conditions. Further, the purpose of this work was also to mathematically describe the process in order to enable better understanding of biodegradation of organic matters in leachate.

Toxicity test with *Vibrio fischeri*, pH value, dissolved oxygen (DO), COD, mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) have been monitored during the experiments. The microscopic analysis was conducted to study the development of activated sludge flocs and its morphology. Leachate samples were found to be biodegradable and more than 72 % COD was removed.

**APPLICATION OF MULTIVARIATE METHODS IN AN
INVESTIGATION OF THE EFFECT OF NO₂, SO₂, CO,
PM₁₀ AND METEOROLOGICAL FACTORS ON OZONE
CONCENTRATIONS IN AN URBAN AREA
PRIMJENA MULTIVARIJANTNIH METODA U
ISTRAŽIVANJU UTJECAJA NO₂, SO₂, CO, PM₁₀ I
METEOROLOŠKIH FAKTORA NA KONCENTRACIJE O₃
U URBANOM PODRUČJU**

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The Principal Component Regression (PCR) is a method that combines linear regression method and PCA technique. This study presents an investigation of the influence of meteorological and air pollutants' variables in predicting O₃ concentrations by using principal component regression method (PCR). The study focuses on the evaluation of the impact of temperature (T), relative humidity (RH), wind speed (WS), wind direction (WD), NO₂, SO₂, CO and PM₁₀ concentrations on ozone variability in the urban atmosphere. The principal component regression method showed that RH, T, WS, the wind vector component that explains air mass movement on the axis east to west, NO₂, CO and SO₂ were responsible for most variations in ozone concentrations ($R^2 \approx 0.82$). Any remaining variability could be attributed to other causes *i.e* parameters that were not monitored in this study. PCR proved to be an effective tool for predicting O₃ concentrations.

INFLUENCE OF DISINFECTION METHODS ON FUNGAL POPULATION OF BARLEY GRAINS

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Fungal contamination of cereals is an important risk factor for health, because some fungi are potentially mycotoxigenic and can cause serious health problems.

Fusarium head blight (FHB) is common disease of cereals all over the world and currently the most important barley diseases in Croatia. *Fusarium* species reduces yield quantity and quality and may also contaminate the grain with fungal toxins -mycotoxins.

The aims of our study were to determine mycopopulation of barley grains with emphasis on *Fusarium* species and to find physical-chemical methods for decontamination and reduction of fungal contamination in barley grains. Barley grains (five cultivars) were collected during 2011 year in four sites of Croatia (Slavonski Brod, Požega, Nova Gradiška and Osijek). Grains are plated on water-soaked filter papers and incubated for seven days at 22 °C under regime of 12 hours light / 12 hours dark. There were 4x100 grains examined for each cultivar and each replication. For decontamination of barley grains we used following physical-chemical methods: grains were rinsed with tap water (30 min), disinfected with 96% ethanol (30 sec.), washed twice in distilled water (1 min.) and put in laminar flow cabinet under UV radiation (24 h). Incidence of *Fusarium* and other fungal species depended of genotype susceptibility, location and applied disinfection method. Average percentage of infected barley grains with *Fusarium* species on samples without disinfection were 25.45 %. The lowest average percentage (6.05 %) of infected grains was on samples after UV disinfection. Generally after UV disinfection isolation frequency of fungi and number of determined genera were lower compared to data obtained after chemical disinfection and without disinfection. Along with *Fusarium* species we isolated fungi from genera *Alternaria*, *Cladosporium*, *Penicillium*, *Aspergillus*, *Rhizopus*, *Epicoccum*, *Gonatobotrys*, *Mucor* and *Helminthosporium*.

**SPEKTROFOTOMETRIJSKO ODREĐIVANJE NITRATA
U VODAMA ZA PIĆE IZ PRIVATNIH ZDENACA
GRADA POŽEGA
SPECTROPHOTOMETRIC DETERMINATION OF
NITRATES IN POTABLE WATER DRAWN FROM
PRIVATE WELLS IN THE CITY OF POŽEGA**

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Water sampling was performed at two specific sites, the first one located in single family houses area at the foot of vineyards, and the other adjacent to Orłjava River, near treated vegetable gardens. Analyses were performed using spectrophotometry, and determination was based on measuring of sample absorbency at 220 nm. The measurement results confirm expectations based on microbiological analyses indicating presence of faecal bacteria having a role in nitrification of ammonia and resulting in increased nitrate concentrations. The wells were built contrary to regulations in vicinity of sewage systems and are obviously permeable to nitrate water pollution. Agrochemical effects on the water are also observed in vicinity of the vineyards. The sampling sites in the city of Požega were selected taking into consideration possible sites of pollution. Increased well water nitrate concentrations in the city of Požega definitely point to increasing environmental and public sanitation problem.

Keywords: Water, private wells, nitrates, sanitary acceptability

**PROCJENA FAKTORA OPASNOSTI NA PRISUTNOST
Legionella pneumophila U TOPLOJ VODI IZ
VODOOPSKRBNOG SUSTAVA
THE ASSESSMENT OF THE RISK FACTORS ON
Legionella pneumophila PRESENCE IN THE HOT WATER
FROM THE WATER SUPPLY SYSTEMS**

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The presence of *Legionella* species in water present a health risk, therefore monitoring and determination of risk factors on *Legionella pneumophila* (*L. pneumophila*) presence is important for water quality preservation. In this paper, risk factors that indicate the presence of *L. pneumophila* in the hot water from the water distribution systems in the Split Dalmatian County were investigated. For that purpose, during 2010 were analysed 79 water samples. The results indicate presence of *L. pneumophila* in the range of 50 – 5000 cfu/L in 44 out of 79 samples. *L. pneumophila* positive samples were categorised in two groups (group 1 – the concentration of *L. pneumophila* was 50 – 750 cfu/L and group 2 – *L. pneumophila* concentrations > 750 cfu/L) and statistically analyzed. The Mg and Cu concentrations expressed as medians were higher in group 2 samples in comparison to group 1 samples, but Ca concentrations were smaller for 3.4 mg/L in group 2 in comparison to group 1 samples ($z = 1.898$; $p = 0.058$). In *L. pneumophila* positive samples higher Fe concentrations and lower values of Zn concentrations were determined. The scientific approach proved the dependence of *L. pneumophila* presence with the concentration of metals and pointed to the potential public health problem.

RASPODJELA OLOVA U ZRAKU, TLU I MORSKOM SEDIMENTU NA ŠIREM SPLITSKOM PODRUČJU LEAD DISTRIBUTION IN AIR, SOIL AND SEA SEDIMENT IN SPLIT AREA

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Characteristics of heavy metals are their accumulation in soils, sediments, seawater, ground water, even in treated wastewaters as threat to the environment and humans. Lead is one of the most toxic heavy metals affecting the environment. It comes into environment through the combustion of fossil fuels and waste from the process of smelting works, leachate from mining pits, from galvanizing plants. The lead content was determined in the air, soil and surface sediments from December 2007. to December 2008. Lead concentration in air were in the range from 0.52 to 241.42 ($\mu\text{g m}^{-2} \text{ day}^{-1}$), with an average value of 24.57 ± 34.44 . In the soil content was found from 11.33 to 66.13 (mg kg^{-1}) and average value of 35.96 ± 15.10 , in the surface sediments ranged from 31.22 to 144.41 (mg kg^{-1}) with average value 67.41 ± 28.42 . In air the highest lead values were determined on a site between two cement factories, and in the soil at the location near roads. In the sea sediment, the highest concentrations were measured in the eastern part of the Kaštela bay. The lead content in the air at all stations was above limit values recommended by the Law on Air Protection (NN178/04), except station between two cement factories where is moderately contaminated. The results obtained for soil and surface sediments in this study were obtained in the ranges of soil in Croatia and sediment in the Adriatic.

INAKTIVACIJA SOMATSKIH KOLIFAGA I FEKALNIH KOLIFORMA KLOROM U POVRŠINSKOJ VODI CHLORINE INACTIVATION OF SOMATIC COLIPHAGES AND FECAL COLIFORMS IN SURFACE WATERS

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Fecal coliforms presence in routine surface water quality monitoring indicates fecal contamination. Somatic coliphages (bacterial viruses) can be used as fecal contamination indicator as well as possible human enteroviruses (frequent waterborne illness causative agents) presence. The aim of this survey was to estimate different chlorine concentrations influence on fecal coliforms and somatic coliphages survival. Fecal coliforms were detected by modified HRN EN 9308-1:2000 method. Somatic coliphages were determined according to HRN EN ISO 10705-2:2008 norm. The lowest used chlorine concentration (0.1 mg Cl₂/L) causes obvious decrease in fecal coliforms number and reduction number of somatic coliphages. At the chlorine concentration of 0.3 mg Cl₂/L and higher, fecal coliforms were no more detected while somatic coliphages were reducing proportionally. With respect to the survey results it can be concluded that somatic coliphages might play a role as a more reliable indicator in surface water quality estimation.

Key words: fecal coliforms, bacteriophages, indicators, resistance, chlorine.

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**ISPITIVANJE MOGUĆNOSTI UKLANJANJA
UGLJIKOVODIKA IZ SITNOZRNOG MATERIJALA
POSTUPCIMA ATRICIJSKOG PRANJA I FLOTACIJE
REMOVAL OF THE ORGANIC POLLUTANT FROM THE
SMALL SIZED PARTICULATE BY ATTRITION
SCRUBBING AND FLOTATION**

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Removal of contaminant by soil washing results in two products: clean soil and sludge. Clean soil contains coarse particles and sand while in sludge, fines and the most of the contaminant are contained. Contaminated sludge requires further treatment and/or disposal. In cases when the feed is composed mostly by fines, or if there are large quantities of material to treat by soil washing, quantity of contaminated sludge can make the simple soil washing inefficient. This paper presents the investigation of attrition scrubbing and flotation for removal of the organic pollutant from the small sized silica and carbonate sand and fines (size grade < 0.1 mm).

Keywords: soil washing, sludge, organics, attrition scrubbing, flotation

**MJERENJE RADONA DETEKTOROM NUKLEARNIH
TRAGOVA LR 115
ENVIRONMENTAL RADON MEASUREMENTS BY LR 115
NUCLEAR TRACK DETECTORS**

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Radon has been classified as a human carcinogen. Since environmental radon on average accounts for about a half of all human exposure to radiation from natural sources, increasing attention has been paid to exposure to radon and its associated health risks in both industrialized and developing countries. Passive radon dosimeters based on LR 115 nuclear track detectors are very attractive for assessment of radon exposure. For developing countries wishing to undertake national radon survey the most appropriate techniques are those making use of LR 115 detectors. These detectors are small, cheap, simple, and non-hazardous and provide an entirely adequate tool for large scale use in assessing levels of radon over several months because of the short – term fluctuations in radon concentrations. In this work, the principles in order to improve the quality and reliability of radon exposure under a quality assurance (QA) program are presented. Also example of how a QA program of radon measurements by LR 115 detectors using the can-technique is well defined and applied. The result shows that, comparing with others detectors is very cheap and simple to use in detection of the radon in agriculture industries.

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**UKLANJANJE AMONIJAKA IZ ANAEROBNO
PROČIŠĆENE OTPADNE VODE
REMOVAL OF AMMONIA FROM EFFLUENT OF
ANAEROBICALLY TREATED WASTEWATER**

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Otpadne vode prehrambene industrije karakterizira visok sadržaj organskih tvari. Takve vode nazivaju se jako opterećene otpadne vode i moraju se pročišćavati za šta se primjenjuju anaerobni biološki postupci pročišćavanja zasnovani na procesu metanskog vrenja. Otpadne vode ove industrije često sadrže veliku količinu organskog dušika koji se u procesu metanskog vrenja prevodi u amonijak, a on, ukoliko se ne ukloni iz otpadnih voda, može aerobnim putem u prirodi ili u aerobnim postupcima pročišćavanja preći u nitrate, koji predstavljaju značajne zagađivače okoliša. Cilj ovog rada je utvrđivanje optimalnih uvjeta za izvođenje postupka uklanjanja amonijaka aeracijom prethodno alkalizirane anaerobno pročišćene otpadne vode. Ogledi su izvedeni na različitim pH vrijednostima otpadne vode pri konstantnom protoku zraka. Rezultati su pokazali da udio amonijaka koji se izdvaja aeracijom značajno raste sa porastom pH vode preko 9, a za potpuno uklanjanje amonijaka optimalan pH je 11-11,5. Uklanjanjem amonijaka smanjuje se i zagađenje vode, izraženo preko KPK, za 45 %. Na temelju dobivenih rezultata dan je prijedlog tehnološkog postupka uklanjanja amonijaka iz anaerobno pročišćene otpadne vode. Ispitana je i mogućnost vezivanja izdvojenog amonijaka u sumpornoj kiselini, ali se pokazalo da je za ispitivanje učinkovitosti u ovom slučaju potrebno izvesti pokuse na poluindustrijskoj razini.

SMANJENJE EMISIJE DUŠIKOVIH OKSIDA (NO_x) IZ POSTROJENJA ZA PROIZVODNJU AMONIJAKA REDUCTION OF NITROGEN OXIDE EMISSIONS (NO_x) FROM AMMONIA PLANT

Tihomir Hajba

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Cilj rada je analiza postojećeg stanja na postrojenju za proizvodnju amonijaka u Petrokemiji d.d. Kutina s posebnim naglaskom na emisije dušikovih oksida (NO_x) iz peći primarnog reformiranja u okoliš. Rezultati istraživanja pokazali su da nakon ugradnje Jedinice za izdvajanje amonijaka i vodika iz ispusnih plinova sintezne sekcije početkom 2009. godine, prosjek srednjih dnevnih emisijskih koncentracija NO_x (kao NO₂) za 2009., 2010. i 2011. godinu, iznosi 456 mg Nm⁻³, uz emisijski faktor 2,186 kg t⁻¹ NH₃. Usporedbom hrvatskog zakonodavstva i zakonodavstva Europske unije uočeno je da će se emisija NO_x (izraženo kao NO₂) i emisijskog faktora održati ispod nacionalnih graničnih vrijednosti emisija (GVE) do 31.12.2015. godine, međutim procjenjuje se da će od 2016. emisija NO_x biti na gornjoj granici, odnosno neće zadovoljiti GVE. Emisijski faktor je već sada na gornjoj granici, a od 31.12.2015. godine neće zadovoljiti niti nacionalne granične vrijednosti emisija. Prema smjernicama najboljih raspoloživih tehnika (NRT) postrojenje ne zadovoljava GVE s obzirom na NO_x, a ulaskom Republike Hrvatske u EU, postrojenje neće biti u okviru GVE zakonodavstva EU. Na temelju teorijskih saznanja i analize prikupljenih podataka predložene su i opisane metode/tehnologije za izdvajanje amonijaka iz niskotlačnog otpadnog plina iz sinteze i rashladnog sistema te metode/tehnologije smanjenja emisija dušikovih oksida iz peći primarnog reformiranja, uzimajući u obzir tehničko-tehnološke značajke postrojenja za proizvodnju amonijaka i proizvodna ograničenja, ciljanu vrijednost emisije NO_x od 100 mg Nm⁻³, lokalna ograničenja te ekonomske čimbenike. Za preciznije podatke o mogućem smanjenju emisija NO_x iz postrojenja za proizvodnju amonijaka, odnosno peći primarnog reformiranja potrebna je detaljnija analiza njezinog rada.

Ključne riječi: dušikovi oksidi (NO_x), membranski reaktor, peć primarnog reformiranja, postrojenje za proizvodnju amonijaka, selektivna katalitička redukcija, selektivna nekatalitička redukcija.

**PROSTORNA I VREMENSKA KLASIFIKACIJA
POKAZATELJA ONEČIŠĆENJA KOMUNALNIH
OTPADNIH VODA GRADA SPLITA
SPATIAL AND TEMPORAL CLASIFICATION
OF POLLUTION INDICATORS OF MUNICIPAL
WASTEWATER IN SPLIT**

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In this paper a set of quantitative descriptive and analytical data of pollution indicators of municipal wastewater of wider Split area were analysed by multivariate statistical technique. Multivariate statistical technique such as cluster analysis (CA), factor analysis (FA) and principal component analysis (PCA) were employed to investigate spatial and temporal classification of pollution indicators on three drain locations over a period of 4 years (2006-2009). The implementation of these analyses required the proceedings in the preliminary study for the selection of treatment technologies and making the project of device and a precondition for setting up the complex mathematical models that will enable an effective control and optimize the process of disposal and wastewater treatment. The obtained results show and explain similarity or dissimilarity between the sampling locations and period of time, identifications of pollution indicators responsible for temporal and spatial variations and hidden factors explaining the structure of the database.

**PRIMJENA MULTIVARIJANTNIH STATISTIČKIH
METODA U OCJENI KVALITETE PODZEMNIH VODA
BRČKO DISTRIKTA BIH
APPLICATION OF MULTIVARIATE STATISTICAL
TECHNIQUES FOR EVALUATION OF GROUNDWATER
QUALITY IN BRČKO DISTRIKT**

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The quality of ground water as a source of drinking water in Brčko Distrikt is regularly monitored. During the five years period (2004-2008), 2560 samples of ground waters were analysed. The mass concentration of cations (Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , Mn^{2+} , NH_4^+) and anions (F^- , Br^- , Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , HCO_3^-), temperature, pH, total hardness, TDS, KMnO_4 , BPK_5 , O_2 and conductivity have been measured using standard analytical methods. To assess the physico-chemical composition of groundwaters, we used multivariate statistical methods of data analysis, viz. cluster analysis, factor analysis and discriminant analysis. Cluster analysis resulted in a dendrogram, where all 92 groundwater sources are divided into a number of clusters, depending on the level of similarity. Factor analysis, using principal components analysis, singled out six factors (Eigenvalue > 1) that explain approximately 79.2 % of total variance. According to the results of multivariate analysis, all groundwater sources were divided into ten groups that are naturally associated. To sum up, the present study reveals new information from the data sets such as patterns of similarity between sampling locations, seasonal behavior of chemical contents and time trends.

Keywords: groundwater quality, water classification, multivariate statistical techniques

**PRIMJENA DIMENZIJSKE ANALIZE ZA ODREĐIVANJE
OVISNOSTI IZMEĐU FENOMENA SORPCIJE
I OMJERA KRUTO/TEKUĆE
DIMENSIONAL ANALYSIS AS A USEFUL TOOL
IN DETERMINING THE RELATIONSHIP BETWEEN
SORPTION PHENOMENA AND THE SOLID/LIQUID
RATIO**

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The performance of zinc removal on natural zeolite has been evaluated relative to the solid/liquid (S/L) ratio in the range from 2.5 to 120 g/l at the constant initial zinc concentration of 3.334 mmol/l. Dimensional analysis was applied to the Freundlich isotherm in order to establish the relationship between sorption of zinc on natural zeolite and the S/L ratio. With the assumption that the total amount of zinc removed on zeolite is a function of equilibrium concentration, solution volume and zeolite amount, the Freundlich isotherm has been converted into the Power-function Freundlich-like Model (PFM). The equilibrium experimental results have been fitted to the PFM model, and the parameters of the model have been determined. In order to test the validity of dimensional analysis, a set of experimental data obtained at a certain solid-liquid ratio were also fitted to the PFM model and Freundlich isotherms. The results show excellent fitting to the PFM model, while the fit to the Freundlich isotherm failed. This indicates that the PMF model is suitable for description of the equilibrium in solid/liquid sorption system independently of the S/L ratio and initial concentration.

Keywords: dimensional analysis, Power-function Freundlich-like Model, natural zeolite, solid/liquid ratio, sorption

ZNANJE UČENIKA MLAĐE ŠKOLSKJE DOBI O ZAŠTIĆENIM PRIRODNIM PODRUČJIMA HRVATSKE KNOWLEDGE OF YOUNGER SCHOOL AGE CHILDREN ABOUT PROTECTED NATURE AREAS IN CROATIA

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Zaštićena područja doprinose očuvanju biološke i krajobrazne raznolikosti osobito rijetkih i ugroženih vrsta te njihovih staništa. U područjima pod raznim oblicima zaštite trajno su ograničene ili zabranjene ljudske djelatnosti koje bi ih mogle ugroziti, a u Republici Hrvatskoj je 447 lokaliteta pod nekom od zakonskih kategorija zaštite. U odgoju za okoliš polazi se od upoznavanja prirodnih znamenitosti kao dijela ukupne prirodne i kulturne baštine. Zato je cilj našeg istraživanja bio odgovoriti na pitanje koliko djeca mlađe školske dobi znaju o zaštićenim prirodnim područjima u Republici Hrvatskoj te koliko su svjesna važnosti zaštite prirode. Istraživanje je provedeno anketiranjem ukupno 63 učenika četvrtih razreda u Osnovnoj školi Vladimira Nazora u Đakovu. Anketa je sadržavala 14 pitanja objektivnog tipa. 49 % ispitanih djece je posjetilo barem jedan nacionalni park u Republici Hrvatskoj. Svi učenici poznaju da su nacionalni parkovi najpotpuniji oblici zaštićenog prostora, a od parkova prirode najpoznatiji su im Lonjsko polje, Medvednica i Kopački rit. Na pitanje zašto ljudi štite prirodu učenici su odgovarali: zato da bude uredna i lijepa, da bi ljudi, biljke i životinje mogli živjeti, zato što žele sačuvati šume, da bi očuvali život te da bude čista i nezagađena. Ukupni rezultati istraživanja pokazuju da je znanje djece mlađe školske dobi o zaštićenim prirodnim područjima u Republici Hrvatskoj oskudno pa je zato potrebno provoditi što raznolikije izvanučioničke aktivnosti s djecom u prirodi te planski provoditi upoznavanje pojedinih zaštićenih prostora u Republici Hrvatskoj. Ove aktivnosti potrebno je provoditi na svim razinama obrazovanja, a za odgoj za okoliš i ukupni održivi razvoj, najvažnije su one koje se provode u rano školsko doba.

UKLANJANJE ORGANSKIH TVARI IZ PODZEMNIH VODA ŽELJEZOVIM KOAGULANTIMA NOM REMOVAL FROM GROUNDWATERS USING IRON COAGULANTS

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Podzemne vode istočne Hrvatske često sadrže prirodne organske tvari (*engl. natural organic matter*, NOM) u koncentracijama koje narušavaju senzorska svojstva vode uzrokujući pojavu nepoželjnih mirisa i okusa vode, no kako se navedene podzemne vode najčešće koriste u svrhu snabdijevanja pučanstva vodom za piće, nemoguće je zanemariti i problematiku prerade takovih voda. Naime, prilikom provođenja neizostavnog postupka dezinfekcije vode za piće klorom ili sredstvima na bazi klora, nastaju kancerogeni dezinfekcijski nusprodukti tzv. trihalogenmetani (THM). Osim toga, povećane koncentracije NOM u vodi mogu doprijeti i narušavanju mikrobiološke kakvoće vode za piće u distribucijskoj mreži. Danas je u praksi niz tehnoloških rješenja kojima se učinkovito mogu ukloniti NOM iz vode ili smanjiti njihova koncentracija, no pri definiranju učinkovitosti procesa, naglasak se stavlja na identifikaciju svojstava i količinu prirodnih organskih tvari u vodi, stoga je nužno optimizirati proces obrade vode u svrhu uklanjanja istih. Uslijed dobre učinkovitosti i ekonomske prihvatljivosti, u praksi se često NOM uklanjaju iz vode metodom koagulacije i flokulacije koja se temelji na doziranju koagulanata, odnosno soli željeza ili aluminijske soli, pri čemu dolazi do destabilizacije NOM, koje se potom filtracijom uklanjaju iz vode. Kako učinkovitost navedene metode prije svega ovisi o karakteristikama sirove vode i vrsti koagulanta, u ovom radu ispitan učinak uklanjanja NOM doziranjem tri vrste koagulanta (FeCl_3 , $\text{Fe}(\text{NO}_3)_3$ i FeSO_4) u podzemne vode s tri različita izvorišta, te njihov utjecaj na potencijal nastanka trihalogenmetana. Ispitivanja su provedena pri pH-vrijednosti voda 7,5 uz dodavanje koagulanata s ukupnom koncentracijom željeza u sirovoj vodi od 1, 2, 3, 4, 5, 6, 7 i 8 mg/L. Rezultati su pokazali da su optimalne koncentracije željeza za uklanjanje NOM između 7 i 8 mgFe/L, dok je potencijal nastanka THM najviše smanjen (do 97 %) doziranjem $\text{Fe}(\text{NO}_3)_3$.

Ključne riječi: podzemne vode, uklanjanje organskih tvari, THM

KAKVOĆA VODE ZA PIĆE GRADA KARLOVCA DRINKING WATER QUALITY IN THE KARLOVAC AREA

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Karlovačka županija po količini prirodnih voda jedna je od najbogatijih regija Hrvatske, dok se grad Karlovac, uslijed položaja na četiri rijeke – Koranu, Kupu, Dobru i Mrežnicu, izdvaja jedinstvenim geografskim položajem. No, usprkos dostupnosti velikih količina površinskih voda, pučanstvo Karlovačke županije kao vodu za piće najčešće koristi podzemne vode pri čemu se najveći dio pučanstva ovog kraja snabdijeva vodom za piće iz vodoopskrbnog sustava grada Karlovca u kojem se podzemna voda obrađuje samo postupkom dezinfekcije, odnosno doziranjem klora, dok se manji dio pučanstva vodom snabdijeva iz privatnih kopanih bunara. Cilj ovog rada bio je praćenje kakvoće vode za piće na području Karlovačke županije utvrđivanjem mikrobioloških i fizikalno-kemijskih parametara. Uzorci vode su uzeti na šest različitih postaja tijekom više mjeseci te su praćene vrijednosti fizikalno-kemijskih parametara (temperatura, mutnoća, boja, pH-vrijednost, provodljivost, oksidativnost, amonijak, nitrati, nitriti, kloridi, mangan i slobodni rezidualni klor) i mikrobioloških parametara (broj kolonija na 37 °C/1 ml i broj kolonija na 22 °C/1 ml, ukupni koliformi, *Escherichia coli* i Enterokoki). Dobiveni rezultati pokazuju da je voda u vodoopskrbnom sustavu grada Karlovca u skladu s zahtjevima Pravilnika o zdravstvenoj ispravnosti vode za piće (NN,47/08), dok vode iz kopanih bunara najčešće ne udovoljavaju odredbama navedenog Pravilnika uslijed povećanih vrijednosti mikrobioloških parametara.

Ključne riječi: Karlovac, kakvoća vode za piće

TESITIRANJE TEHNIČKIH SUSTAVA U ZAŠTITI BILJA PREMA EUROPSKOJ NORMI EN 13790 TESTING TECHNICAL SYSTEMS IN PLANT PROTECTION ACCORDING EUROPEAN STANDARD EN 13790

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U cilju prilagodbe hrvatskih obiteljskih poljoprivrednih gospodarstava na novo zakonodavstvo Europske unije, obavljena su predavanja i testiranja tehničkih sustava u zaštiti bilja financirana sredstvima Nizozemske darovnice (TF070378), koju su proveli djelatnici Zavoda za mehanizaciju Poljoprivrednog fakulteta u Osijeku. U programu sudjeluje 17 poljoprivrednih udruga sa prostora Slavonije i Baranje. Cilj ovih predavanja bio je obučiti rukovatelje tehničkih sustava u zaštiti bilja za rad sa istim te testirati njihove strojeve i ukazati im na greške koje se trebaju ispraviti. U EU je na snazi direktiva 2009/128/EC i 2006/42/EC kojima je temelj EN 13790 (I,II) standard za testiranje tehničkih sustava u zaštiti bilja. Direktiva se prvenstveno odnosi na smanjenje onečišćenja okoliša s pesticidima pravilnim radom tehničkih sustava u zaštiti bilja. Ulaskom Hrvatske u EU ove direktive postaju aktualne te im se polako treba pridavati značaja.

Ključne riječi: tehnički sustavi u zaštiti bilja, rukovatelji, testiranje, EN 13790 standard

MONITORING VODOSTAJA POVRŠINSKIH VODA U PARKU PRIRODE KOPAČKI RIT MONITORING OF SURFACE WATER LEVEL IN KOPAČKI RIT NATURE PARK

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Park prirode Kopački rit jedno je od najvažnijih i najočuvanijih močvarnih staništa u Europi koje karakterizira, i posebnost osigurava, obilje vodene mase tijekom cijele godine koja na područje Parka prirode Kopački rit dopijeva iz rijeka Dunav i Drava. Velike vodene površine tijekom više stoljeća omogućile su i veliku biološku raznolikost ovog područja te je područje Parka prirode Kopački rit od 1993. godine uvršten u Popis močvarnih i vlažnih područja od međunarodnog značaja, sukladno odredbama Ramsarske konvencije. Na iznimnu biološku raznolikost Kopačkog rita ukazuju i rezultati višegodišnjeg monitoringa prema kojima je na ovom području zabilježeno 446 biljnih vrsta, 44 vrste riba, a povremeno ili stalno se gnijezdi 144 vrste ptica. S ciljem praćenja utjecaja vodostaja rijeke Dunav i rijeke Drave na razine površinskih voda na području Parka prirode Kopački rit, 2009. godine uspostavljen kontinuirani monitoring, odnosno bilježenje vodostaja na području Kopačkog rita na jednoj mjernoj postaji (CS Tikveš) pri čemu se ujedno redovito bilježe i vodostaji rijeke Dunava na tri mjerne postaje (Batina, Apatin, Aljmaš) i rijeke Drave na jednoj mjernoj postaji (Osijek). Monitoring vodostaja na području Parka prirode Kopački rit je sastavni dio Plana upravljanja Parkom prirode Kopački rit koji je temeljni upravljački dokument Javne ustanove „Park prirode Kopački rit“. U ovom radu prikazani su i uspoređeni vodostaji rijeke Dunava i Drave s vodostajima na području Kopačkog rita tijekom dvogodišnjeg razdoblja (2010. – 2011.), a dobiveni podaci su korišteni za procjenu utjecaja promjene količine vodene mase na ekosustav zaštićenog močvarnog područja Parka prirode Kopački rit.

Ključne riječi: Park prirode Kopački rit, vodostaj, površinske vode

ODNOS UČENIKA MLAĐE ŠKOLSKE DOBI PREMA ZAŠTITI OKOLIŠA YOUNG LEARNERS' ATTITUDE TO ENVIRONMENT PROTECTION

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Education for the environment begins when the child experiences its first contact with nature and should continue systematically during school time. As the ecological consciousness is closely related to emotions and the knowledge, our main goal in this investigation was to find out the knowledge level of young learners about ecology and their attitude to environment protection. The investigation was conducted in primary school Ivana Brlić Mažuranić in Koška on a sample of 72 young learners of the first, the second, the third and the fourth grade. An anonymous questionnaire consisted of 12 questions. The results showed that 94 % of pupils of the first grade know about possibilities of preservation the environment, 82 % of pupils of the first and the second grade believe that it is correct to sort the garbage, all pupils from the third grade are ready to act ecologically, 88 % of pupils of the third and the fourth grade are familiar with the ways of nature and environment protection from wastewater and air pollution, the fourth grade pupils can list more protected plants and animals than the third grade pupils, girls were 2 % better in questionnaire than boys, the fourth grade pupils offered more qualitative answers to the question what environment protection is than other investigated pupils. It can be concluded that our investigation has shown a high level of environmental awareness which was shown by pupils of lower school grades in primary school Ivana Brlić Mažuranić in Koška. We can emphasize that developing of the ecological consciousness is present among young learners in a primary school mostly due to teachers who hardly and devotedly work on a proper education for the environment.

SUSRET MLADIH KEMIČARA
MEETING OF YOUNG CHEMISTS

„NA LIJEPOM PLAVOM DUNAVU“ „THE BEAUTIFUL BLUE DANUBE“

Nataša Vinković i učenici Gimnazije Vukovar

Gimnazija Vukovar, Šamac 2, 32000 Vukovar

Na natječaju „Čiste hrvatske obale“, učenici Gimnazije Vukovar sudjeluju s projektom „Na lijepom plavom Dunavu“. Cilj nam je vratiti Dunavu stari naziv „lijepi plavi Dunav“ te ekološki osvijestiti građane grada Vukovara koliko je otpad štetan za prirodu, grad i ljudsko zdravlje. Neke od metoda provođenja projekta su: posjet Institutu hrvatskih voda i Vodovodu grada Vukovara te sakupljanje informacija o trenutnom stanju vode koje smo koristili za izradu letaka. Proveli smo anketu u školi i gradu te se upoznali s mišljenjem i stupnjem ekološke osviještenosti stanovništva. Vrhunac projekta je organiziranje štanda u centru grada te izvođenje pokusa. Dijelili smo letke, objašnjavali građanima stanje vode te saznali nove informacije o gradnji filtera i djelovanju športsko-ribarskih udruga. Organizirali smo i eko dan u školi. Svoje planove smo ostvarili te vjerujemo kako polako, ali sigurno vraćamo stari naziv... na lijepom plavom Dunavu.

„PLATNENE PELENE“ „CLOTH DIAPERS“

Nataša Vinković i učenici Gimnazije Vukovar

Gimnazija Vukovar, Šamac 2, 32000 Vukovar

Učenici Gimnazije Vukovar tijekom ove školske godine izradili su projekt o platnenim pelenama. Cilj je bio ukazati na posljedice do kojih dolazi uporabom jednokratnih pelena, a koje bi se mogle znatno umanjiti korištenjem platnenih pelena. Tijekom istraživanja u koje je uloženo puno truda upozorili smo na ekološke probleme te na prihvatljivije izbore proizvoda koji utječu na okoliš- na sve nas. Projekt je zaintrigirao mnoštvo te smo na taj način barem malo povećali ekološku svijest stanovnika grada Vukovara.

VOLUMETRIJSKO ODREĐIVANJE VITAMINA C **VOLUMETRIC DETERMINATION OF VITAMIN C**

Nataša Mišić, Nevena Marin, mentor: Đurđevka Pecikozić

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L-ascorbic acid has an activity of a vitamin and is known as the Vitamin C. When the lack of Vitamin C is present in our body it is seen in decreased resistance to infectious diseases. In most animals the Vitamin C can be synthesized from glucose or other compounds. Human body is incapable of doing this. The Vitamin C is a nutritive substance that we take into our body with food. The richest sources of Vitamin C are fruit and vegetables. In case of various flu and other diseases epidemic it is recommended for humans to take as much as possible of this Vitamin. The quantity of Vitamin C in lemon, orange and industrial lemon- and orange-tasting beverages is determined on volumetric-basis. It was titrated by iodide solvent with added starch used as indicator. The values acquired by means of titration were mathematically worked out. The given results show that an orange contains more Vitamin C than the same quantity of lemon. The beverages contain the quantity of Vitamin C as declared. If we want to take into our body the recommended quantity of Vitamin C (75-90 mg) one should eat at least 200g of orange or 284 g of lemon or drink at least two bottles of beverages on a daily basis.

Keywords: L-ascorbic acid, Vitamin C, lemon, orange

THE INFLUENCE OF TEMPERATURE ON DECOMPOSITION OF VITAMIN C UTJECAJ TEMPERATURE NA RASPAD VITAMINA C

Olivera Rudić, Violeta Mazur, mentor: Đurđevka Pecikozić

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Chemical kinetics studies the velocity of chemical reactions, conditions influenced by, and mechanical reactions thereto. L-ascorbic acid or Vitamin C is a very important nutritive ingredient that we take into our body with food. Temperature and moisture have great influence on the stability of Vitamin C. We tested the Vitamin C mass alteration in connection with the change of temperature. In this respect water solvents of the PLIVA Vitamin C tablets of various concentrations were placed at high and low room temperatures. In order to establish the Vitamin C mass, we used the method of neutralisation of weak acid ($C_6H_8O_6$) with strong base (NaOH). The final titration point was determined potentiometrically. Such results acquired by means of potentiometric titration were mathematically and graphically worked out. The given values show that the Vitamin C mass in water solvents is decreased by boiling, freezing, or keeping on a room temperature for a longer time. On the basis of such research, it has been concluded that such products should be stored in appropriate way, and used until validity, and not used products should be disposed of in appropriate way.

Key words: chemical kinetics, temperature, decomposition, Vitamin C

**PRAĆENJE KOLIČINE OTOPLJENOGA KISIKA U VODI
RIJEKE DRAVE U VREMENU OD SVIBNJA DO RUJNA
2012. GODINE
MONITORING THE AMOUNT OF DISSOLVED OXYGEN
IN THE WATER OF THE RIVER DRAVA IN THE PERIOD
BETWEEN MAY AND SEPTEMBER 2012**

Josipa Bojčić, Martin Kovačević, Zlatna Lončar, Nada Pitinac

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Otopljeni je kisik jedan od najvažnijih pokazatelja ekoloških uvjeta u vodi, te kvalitete površinskih voda. Definira se količinom otopljenoga kisika u $\text{mg O}_2/\text{l}$ vode i zasićenošću vode kisikom koja se dobije računski iz omjera izmjerene vrijednosti i teorijske vrijednosti otopljenoga kisika pri istim uvjetima tlaka i temperature. Bez kisika ili u uvjetima nedovoljne količine kisika, uvjeti za život u vodi su ograničeni ili ih uopće nema. Minimalna granična vrijednost za duži vremenski period je 4 do 5 $\text{mg O}_2/\text{l}$. Topljivost kisika u vodi ovisi o parcijalnom tlaku kisika u zraku, temperaturi vode i salinitetu. Pri tlaku zraka 1 bar i temperaturi vode 0°C uz zasićenje od 100 %, topljivost kisika je 14,57 mg/l . Na vrijednosti količine otopljenoga kisika utječu i čimbenici kao što su onečišćenost vode, manjak ili višak svijetla, protok vode i doba dana. Godišnje i dnevne varijacije količine otopljenoga kisika najviše ovise o tlaku zraka i temperaturi vode. Kisik u vodu dolazi iz atmosfere - difuzijom, mehaničkim putem – aeracijom, te fotosintezom autotrofnih biljaka. Na dinamičku ravnotežu kisika utječe i potrošnja kisika u vodi. Kisik se troši disanjem biljnih i životinjskih organizama i drugim oksidacijskim procesima u vodi, koji su posljedica ispuštanja komunalnih otpadnih voda i voda iz tehnoloških procesa, u tekuće vode. Količina otopljenoga kisika može se odrediti: Winklerovom jodometrijskom metodom, spektrofotometrijski i elektrokemijskom metodom. U radu su ispitivani parametri količina otopljenoga kisika (mg/l) i zasićenje kisikom (%) u vodi rijeke Drave, elektrokemijskom metodom, u vremenu od svibnja do rujna 2012. godine. Sve izmjerene vrijednosti količine otopljenoga kisika veće su od 7,00 mg/l , a zasićenje kisikom u intervalu od 80 % do 110 %. Prema izmjerenim vrijednostima navedenih pokazatelja režima kisika, voda rijeke Drave mogla bi se svrstati prema klasifikaciji u vode I. vrste. Kako bismo to mogli sa sigurnošću tvrditi, trebalo bi praćenjem obuhvatiti i ostale pokazatelje režima kisika BPK_5 i KPK_{Mn} .

OSNOVE BELOUSOV-ZHABOTINSKY REAKCIJE BASICS OF BELOUSOV-ZHABOTINSKY REACTION

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Belousov-Zhabotinsky reakcija je jedna od najpoznatijih oscilacijskih reakcija uopće u znanosti. Danas, još uvijek, predstavlja veliki izazov svima koji je istražuju ili proučavaju njenu primjenu i kao takva je predmet malog broja izuzetno zahtjevnih istraživanja. Kao oscilacijsku reakciju ju karakterizira period oscilacije u kojem se, u pravilnim razmacima, mijenjaju koncentracije bromatnog, bromitnog i bromidnog iona zajedno s koncentracijom malonske kiseline i metalnog katalizatora. Posljedica oscilacije koncentracija je najpoznatija osobina Belousov-Zhabotinsky reakcije – valovi. Kako valovi, tako i oscilacije koncentracija ovise o nekoliko aspekata: početnim koncentracijama, temperaturi reakcijske smjese i heterogenosti ili homogenosti sustava. U ovom radu su se istražili povijesni počeci Belousov-Zhabotinsky reakcije te prikazao kemijski pogled na reakciju koji prikazuje kako se reakcija odvija i zašto, fizikalni pogled koji, između ostaloga, eksperimentalno daje odgovore na pitanje kako temperatura, početna koncentracija malonske kiseline i količina katalizatora feroina utječu na razvoj Belousov-Zhabotinsky reakcije. Isto tako, u radu je predstavljen i matematički pogled na reakciju koji je dosta kompliciran, ali pokazuje težnju kroz povijest za pojednostavljanje, te biološki pogled u kojem se zapravo vidi svekolika primjena Belousov-Zhabotinsky reakcije od boljeg shvaćanja ponašanja nekih mikroorganizama preko sličnosti s ventrikularnom fibrilacijom pa čak i do nastanka života na Zemlji.

Ključne riječi: Belousov-Zhabotinsky reakcija, oscilacijske reakcije, kinetika kemijskih reakcija

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ALKALOIDI – IZOLACIJA PIPERINA IZ PAPRA

ALKALOIDS – ISOLATION OF PIPERINE FROM PEPPER

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Alkaloidi su vrlo rasprostranjeni u biljnom svijetu. Proizvodi su metabolizma biljaka no njihova uloga nije u potpunosti razjašnjena. Mnogo izazivaju značajne fiziološke efekte kod čovjeka, pa su ih kao takve tvari poznavali i stari narodi. Mogu djelovati kao stimulansi, hipnotici, psihodelične droge ili kao narkotici. Prirodni su organski spojevi koji sadrže jedan ili više atoma dušika u heterocikličkom prstenu. Baznih su svojstava. Netopljivi su u vodi, a topljivi u anorganskim kiselinama i u organskim otapalima. Njihove su soli krute, dobro topljive u vodi, a netopljive u organskim otapalima. Danas je poznato više od 2500 vrsta alkaloida što ih čini najbrojnijom skupinom prirodnih spojeva. Piperin je glavni sastojak papra. Papar je začinska biljka iz porodice piperaceae, čiji su plodovi, zbog alkaloida piperina, ljutog okusa. Višegodišnja je tropska penjačica koja se penje po drveću. Može narasti 5 do 10 metara u dužinu. Stablo joj je glatko s tamnozelenim jajolikim, na kraju ušiljenim listovima i malim cvjetovima iz kojih se razvijaju okrugli plodovi. Plodovi su u početku zeleni, a sazrijevanjem po crvene. Rastu u skupinama od 20 do 30 bobica nanizanih jedna pored druge. Domovina papra su vlažne prašume zapadne indijske obale, nazvane Malabar. Papar je bogat alkaloidima. Pikantan okus i ljutinu mu daju alkaloidi piperin, piperetin, piperylin i chavicin. Bijeli papar sadrži oko 2,5 % eteričnih ulja, a u zelenom i crnom papru njihov je sadržaj do 4,8 %. Koristimo ga kao začim, ali su poznata i njegova ljekovita svojstva. Njegova ljekovita svojstva pripisuju se alkaloidu piperinu koji utječe na bolju apsorpciju mnogih nutrijenata. Studije su pokazale i njegovo antikancerogeno djelovanje (rak pluća i melanom). U radu je provedena ekstrakcija piperina iz zelenog, crnog, crvenog i bijelog papra. Ekstrakcija je provedena refluksiranjem s etilnim alkoholom. Vruća reakcijska smjesa je nakon refluksiranja filtrirana i podvrgnuta destilaciji. Ostatku je dodan natrijev hidroksid pri čemu se talože kristalići piperina. Dobiveni kristalići piperina su nakon odisavanja isprani otopinom natrijeva karbonata, zatim vodom do neutralne reakcije i na kraju eterom. Nakon sušenja određen je udio piperina u uzorcima. Crni papar sadrži 5,65 % piperina što je najviše u odnosu na druge vrste.

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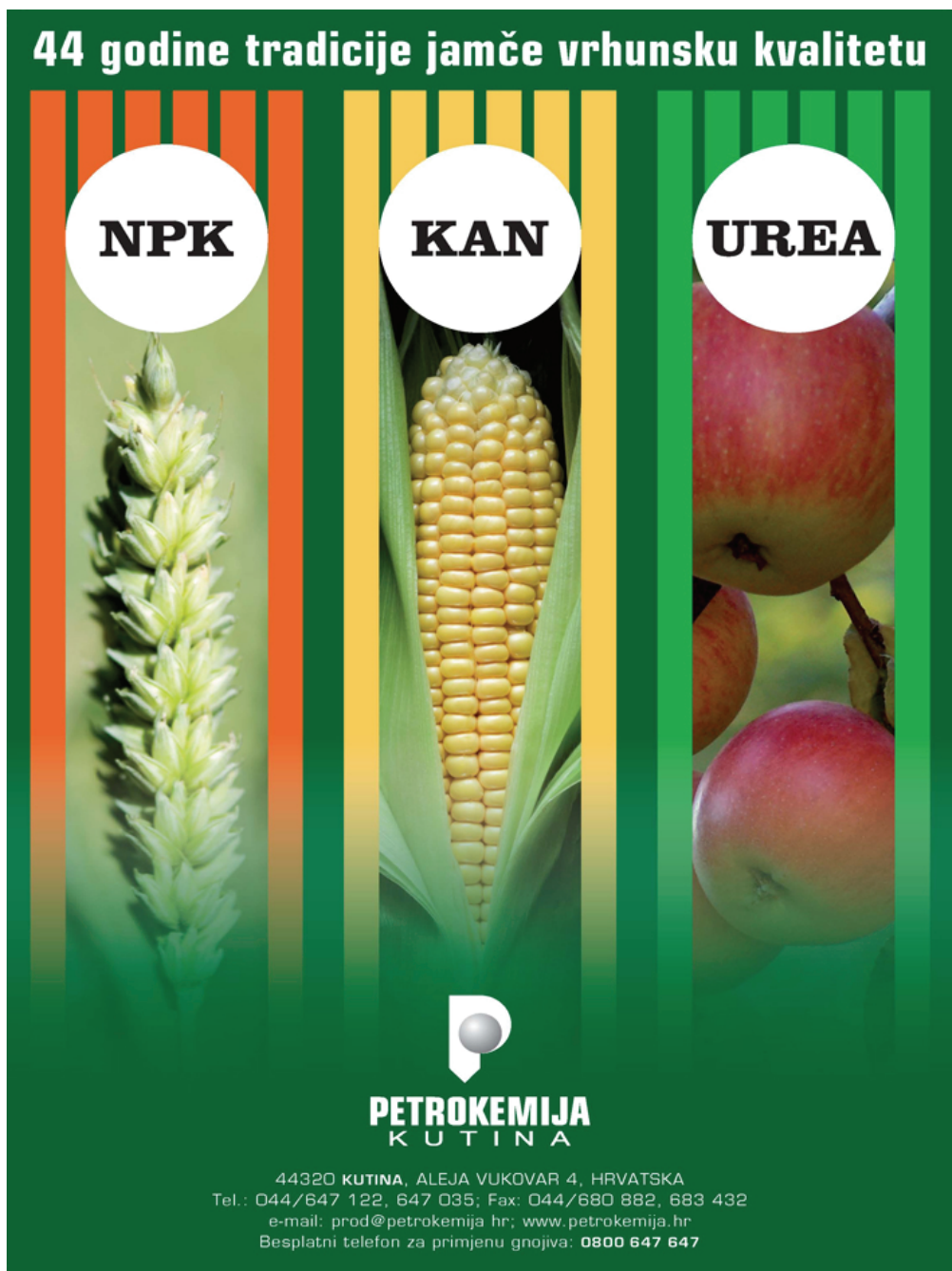
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