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Intensive Lecture Course

Faculty of Natural Sciences and Mathematics
Institute of Chemistry
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From Molecules to Functionalised Materials

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16th – 20th March 2011
Skopje
Republic of Macedonia

Scientific Programme

Wednesday, March 16th

arrival of participants in Skopje

Thursday, March 17th

Location: *Institute of Chemistry,
Conference Hall, room 104*

10:00 - 12:00 Kick-off meeting
for coordinators of the SOE project

10:00 – 12:00 Tour around Labs in the Institute
of Chemistry *for student participants*

Location: *Institute of Chemistry,
Lecture room 124*

12:00 - 12:15 Opening session

12:15 - 13:15 Prof. Dr. Trajče Stafilov
*Detection of trace elements in minerals with atomic
absorption spectroscopy*

13:15- 15:15 Lunch

15:15 – 16:15 Ass. Prof. Dr. Petre Makreski
*Vibrational Spectroscopy and X-ray Powder
Diffraction in the Study of Silicate Minerals -
Advantages and Disadvantages of Each
Technique*

16:15 - 17:15 Ass. Prof. Dr. Rubin Gulaboski
New aspects into the chemistry of coenzym Q

17:15 – 17:45 Coffee break

Location: *Institute of Chemistry,
Amphitheater*

18:00 - 19:30 Chemical spectacle
“The Happy Chemists Group”

Friday, March 18th

Location: *Institute of Chemistry,
Lecture room 124*

9:00 - 10:00 Ass. Prof. Dr. Vladimir Ivanovski
*IR reflectance techniques and their application in
surface chemistry investigations*

10:00 - 11:00 Lect. Dr. Luiza Gaina
*Organic synthesis following the green chemistry
principles*

11:00 - 11:30 Coffee break

11:30 - 12:30 Prof. Dr. Blaga Radovanovic
*Methods for measurement of total antioxidant capacity
of nutritional samples*

12:30 – 14:30 Lunch

14:30 - 15:30 Prof. Dr. Evamarie Hey-Hawkins
Phosphorus - the Devil's Element?

15:30 - 16:30 Teach. Ass. MSc. Ahmed Jashari
Synthesis of Novel Diazo Coupled Coumarins

Saturday, March 19th

Location: *Institute of Chemistry,
Lecture room 124*

8:00 - 10:00 Student presentations
(students from Macedonia)

10:00 - 10:30 Coffee break

10:30 - 12:30 Student presentations
*(students from Germany, Romania, Serbia
and Kosovo)*

12:30 - 14:30 Group Lunch

14:30 - 17:00 Excursion to ancient city
Stobi

Sunday, March 20th

departure of participants



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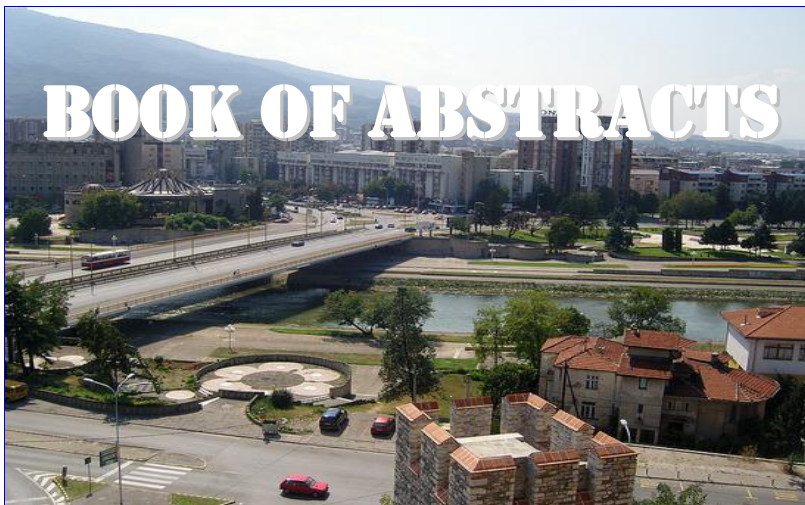


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16th – 20th March 2011
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Republic of Macedonia

LECTURES

DETERMINATION OF TRACE ELEMENTS IN MINERALS BY ATOMIC ABSORPTION SPECTROMETRY

Trajče Stafilov

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The knowledge of the presence of trace elements incorporated in the structure of natural minerals could help to answer on many questions about mineral deposit formation, its physical and chemical properties, crystalline deformations, *etc.* Because trace elements present in the natural structure basically change the primary physical and chemical characteristics of the minerals, they may limit its application for many useful purposes. Therefore, development of appropriate methods for determination of trace elements in mineral matrices has a great importance. Different methods for trace element determination in various types of minerals by using of atomic absorption spectrometry will be presented. In order to avoid matrix interference and because of the very low concentration of trace elements in minerals, it is necessary to separate and concentrate these elements from the samples. Different methods applied for this purpose (extraction, ion exchange, precipitation, etc.) will be also presented. The examples of the application of atomic emission spectrometry with inductively coupled plasma (AES-ICP) and neutron activation analysis (NAA) will be also given.



Vibrational Spectroscopy and X-ray Powder Diffraction in the Study of Silicate Minerals – Advantages and Disadvantages of Each Technique

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A plethora of techniques for identification and characterization of minerals and impurity detection have been developed during the last few decades. X-ray powder diffraction (XRPD), Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy are some of the mostly used techniques for those purposes. The techniques exhibit their own advantages and imperfections and therefore it is strongly recommendable to use them complementary rather than competitive. Sometimes, however, it is necessary to use only one of the above mentioned (or other) techniques.

Here, some of the advantages and limitations when XRPD, FTIR and/or Raman vibrational spectroscopy are used separately in the process of the mineral detection, identification, discrimination and characterization will be comparatively presented. The studied mineral samples are collected from various localities within the Republic of Macedonia. The case studies on the mineral representatives from nesosilicate¹⁻³ [almandine, $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$; spessartine, $\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$; zircon, ZrSiO_4 ; olivine, $(\text{Mg,Fe})_2\text{SiO}_4$], sorosilicate⁴ [epidote, $\text{Ca}_2\text{Al}_2(\text{Fe}^{3+},\text{Al})(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$], cyclosilicate⁵ [tourmaline, $\text{Na}(\text{Fe,Mg})_3\text{Al}_6(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{OH})_4$, beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$], inosilicate⁶ [Fe-johannsenite, $\text{Ca}(\text{Fe,Mn})\text{Si}_2\text{O}_6$; rhodonite $(\text{Mn,Ca})\text{MnSi}_2\text{O}_6$; glaucophane, $\text{Na}_2(\text{Mg,Fe}^{2+})_3(\text{Fe}^{3+},\text{Al})\text{Si}_8\text{O}_{22}(\text{OH})_2$, tremolite–actinolite, $\text{Ca}_2(\text{Mg,Fe}^{2+})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$], and phyllosilicate⁷ group [phlogopite, $\text{KMg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{F,OH})_2$; clinocllore (sheridanite), $(\text{MgFe})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$] will be presented.

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NEW ASPECTS INTO THE CHEMISTRY OF COENZYME Q

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Coenzyme Q10 (CoQ10) and its analogues are lipid-soluble compounds, indispensable for optimal functioning of almost all living organisms. Many of them are used as antioxidants, while acting as main electron mediators in the mitochondrial electron-transport chain (ETC). The primary function of these compounds is to transfer electrons along the ETC and protons across the inner mitochondrial membrane (IMM). The concomitant proton gradient across the IMM is essential for ATP production. Using voltammetry, UV-VIS spectroscopy, electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) we analyzed the structural and functional changes of CoQ10 and its analogs induced by CYP450 enzyme or by concentrated sodium hydroxide (NaOH). We found that both CYP450 and NaOH can cleave the C-O bond of the methoxy groups located on 2,3-positions in the quinone ring, leading to creation of 2,3 dihydroxy forms of COQ. The newly created products have much stronger antioxidant properties than their parent quinones and upon reduction they can effectively bind and transfer Ca^{2+} and other earth-alkaline cations across biomimetic artificial membranes. The potential application of these new vitamins is seen in the field of medicine, pharmacy and cosmetic industry.

Keywords: coenzyme Q, calcium transfer, antioxidants, EPR, voltammetry, vitamins

References: Rubin Gulaboski, Ivan Bogeski, Reinhard Kappel, Markus Hoth, Benzoquinones based antioxidants, European Patent Office, Munich 2010 (PATENT).

IR REFLECTANCE TECHNIQUES AND THEIR APPLICATION IN SURFACE CHEMISTRY INVESTIGATIONS

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IR reflectance techniques are non-destructive, oriented towards investigation and characterization of sample surface in respect to its vibrational, dielectric, optical and orientation properties. Most important IR reflectance techniques are the Specular Reflectance, Attenuated Total Reflectance (ATR) and Diffuse Reflectance IR Spectroscopy (DRIFT), each with its specific field of application. The physical basics of the reflection (specular or total) are described by the Fresnel and Maxwell's equations while for the scattering of the radiation in DRIFT technique, the Mie scattering theory and the phenomenological Radiation transfer equations should be taken into account. Additional opportunities are opened if the Specular Reflectance technique is enhanced using polarized light. Analysis of vibrations of particular molecular species and orientation of their transition dipoles in the crystals possessing different symmetries is then possible. ATR technique is shown to be applicable in the investigation of different sorts of specimens: liquids (including water solutions), solids, and applying polarized light in the investigation of single crystals. DRIFT technique is applied for the in-situ investigation of powders and physisorbed or chemisorbed molecular layer/s on them. This technique can be used e.g. in investigation of molecular layers possessing catalytic properties on different adsorbents.

Keywords: IR specular reflectance spectroscopy, DRIFT, ATR, surface investigation, polarized light

ORGANIC SYNTHESIS FOLLOWING THE GREEN CHEMISTRY PRINCIPLES

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The importance of minimizing the impact that chemical processing produces on the environment is growing, with an increased appreciation of the need to reduce pollution and depletion of our finite environmental resources. Optimal use of material and energy, and an efficient waste management can be recognized as important factors for environmental protection. Industrial chemistry is widely adopting the concept of "Green Chemistry" to meet the key scientific challenges of protecting human health and the environment while simultaneously achieving commercial profitability. Some of the important alternative tools include the use of microwaves (MW) ovens as alternative source. The short reaction times and the expanded reaction range provided by MW-assisted synthesis make it ideal to meet the increased demands in industry, particularly in the pharmaceutical industry [1-5].

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- [4] Gaina L, Cristea C, Moldovan C, Porumb D, Surducan E, Deleanu C, Mahamoud A, Barbe J, Silberg IA, *International Journal of Molecular Sciences*, 8(2), 70-80, **2007** [5] Gaina L, Csampai A, Turos G, Lovasz T, Zsodos-Mady V, Silberg IA, Sohar P, *Organic & Biomolecular Chemistry*, 4(23), 4375-4386, **2006**



METHODS FOR MEASUREMENT OF TOTAL ANTIOXIDANT CAPACITY OF NUTRITIONAL SAMPLES

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Antioxidants play an important role in the body's defence system against reactive oxygen species. There is growing scientific evidence associating antioxidant rich products with a lower incidence of cardiovascular disease, cancers and age-related degenerative processes. Biologically active compounds may contribute to the health potential of natural products. This work proposes a new approach on measuring the antioxidant capacity of phenolic compounds and vitamin C in natural samples (grape, fruit, vegetable, wine, beer), as some synthetic antioxidants. It is based on its inhibition effect on the reaction between hydrochloric acid, bromate and methyl orange (HBM). Proposed HBM assay involve addition of a known excess of bromate and methyl orange to sample in an acid medium, and measurement of absorbance at 505 nm 5 min after addition of the last drop of the bromated solution. The presence of phenolic compounds in the medium causes a slower reaction. The reliability of the new method was established by parallel determination by the 2,2'-diphenyl-1-picrylhydrazyl (DPPH·) assay. In this method the antioxidant capacity can be expressed as the amount of sample needed to quench certain amount of DPPH·. The decrease in the absorbance at 517 nm is taken as a measure of the extent of radical-scavenging. Results show that HBM inhibition assay was simple method that can measure the total antioxidant capacity level directly from plant extracts.

Keywords: antioxidant capacity, spectrophotometric methods, natural samples.

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PHOSPHORUS — THE DEVIL'S ELEMENT?

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“Phosphorus was discovered by the alchemists, researched by the early chemists, exploited by the industrialists of the nineteenth century and abused by the combatants of the twentieth. Its capacity for evil cursed all who tried to exploit it, from the would-be murderer to the worldwide manufacturer. But set against this tale of woe are a few remarkable benefits that phosphorus brought; and it is an important ingredient in many of the things we use in our everyday lives.”^[1]

The chemical element phosphorus was discovered by the German alchemist Hennig Brand in 1669 on attempting to create the fabled Philosopher's stone through distillation of urine. He produced the white form of phosphorus, which glows upon exposure to oxygen. This characteristic brought its name which means “light-bearer” in Greek. Until the process for manufacturing the far less flammable and toxic red phosphorus was discovered, the use of white phosphorus resulted in many murders, suicides and accidental poisonings.

Phosphorus is the sixth most abundant element in the human body next to calcium. About 85% of phosphorus in the body can be found in bones and teeth. It is an essential element for metabolic processes and a component of DNA, RNA and ATP. Phosphorus is widely used in friction matches, fireworks, fertilisers, food additives, detergents and as starting material for other compounds like flame retardants, pharmaceuticals, pesticides and insecticides. The production and stockpiling of chemical weapons (neurotoxins) was outlawed by the Chemical Weapons Convention in 1997.

Catalytic processes play an important role in the pharmaceutical and chemical industry, where more than 85% of all chemical products are produced by catalytic reactions. Phosphine ligands are extremely important in homogeneous catalysis, especially chiral ones which can improve significantly the efficiency, specificity and selectivity of catalysts.

[1] John Emsley, *The 13th Element*, John Wiley & Sons, Inc. 2000



SYNTHESIS OF NOVEL DIAZO COUPLED COUMARINS

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Coumarin and its derivatives from natural products, either semi-synthetic or synthetic, have been shown to possess a remarkably broad spectrum of biological activity including antibacterial, antifungal, anticoagulant, anti-inflammatory, and anti-HIV activity[1-3]. Also, remarkable antitumor activities of some coumarins were reported[4-5].

In the course of our work on synthesis of some new coumarin derivatives, electrophilic substitution reactions of 4-hydroxycoumarin with some diazonium salts prepared from amino-heterocyclic compounds were investigated. First, the diazonium salts were obtained in aqueous media at low temperature (≈ -10 °C) from various heterocyclic amines: 2-aminothiazoles, 2-aminobenzothiazole, 2-aminoisoxazole and 2-aminotriazole, as for as 2-amino-, 2-amino-3-methyl-, 2-amino-5-chloro-, 2-amino-5-bromo- and 2-amino-3,5-dichloropyridine. Subsequently, basic aqueous solution of 4-hydroxycoumarin was added, followed with occurrence of intensively colored precipitate. Substitution takes place at position 3 as expected and some novel derivatives of 4-hydroxycoumarin were obtained in moderate yields. The structures were confirmed by IR, MS, ¹H-NMR and ¹³C-NMR spectra.

Keywords: 4-hydroxycoumarin, electrophilic substitution, diazo coupling, anti-cancer activity.

References:

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STUDENT PRESENTATIONS



STUDYING THE ANTIOXIDANT CAPACITY OF ASCORBIC ACID BY MEANS OF CYCLIC VOLTAMMETRY AND CHRONOAMPEROMETRY: FURTHER PERSPECTIVE OF THE RESEARCH

Galaba Naumova, Tanja Atanaskova, Valentin Mirčeski

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Vitamin C is a water soluble, naturally occurring reducing agent with antioxidant capacity that participates in many biochemical redox processes. The antioxidant capacity of vitamin C by measuring the rate of the homogeneous redox reaction with ferrocenedimethanol cation has been studied in an aqueous phase by means of cyclic voltammetry and chronoamperometry. Ferrocenedimethanol cation was electrochemically *in situ* generated at the surface of glassy carbon electrode by electrochemical oxidation of ferrocenedimethanol. Thus, the ferrocenedimethanol cation serves as a redox mediator for catalytic oxidation of ascorbic acid. The redox reaction proceeds with the highest rate in a slightly alkaline medium at pH 8.

The further objective of the research is to determine the antioxidant capacity of vegetable oils by the described method based on ferrocenedimethanol cation, as well as by direct oxidation of oil droplets immobilized on glassy carbon electrode surface. It is expected that vegetable oils possess a high resistance to the oxidative degradation due to the presence of significant amounts of antioxidative compounds.

Keywords: Vitamin C, ferrocenedimethanol, antioxidant capacity, vegetable oils, cyclic voltammetry, chronoamperometry.

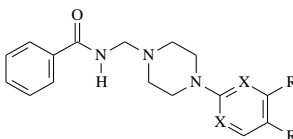


SYNTHESIS OF [(4-ARYLPIPERAZINYL)METHYL]BENZAMIDES AS POTENTIAL SEROTONIN 5-HT RECEPTOR AGONISTS

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Due to the extremely high physiological and pharmacological scope of activity of piperazine and its derivatives, in recent decades there has been a huge trend for their synthesis. The piperazine scaffold has been classified as a privileged structure, molecule that is capable of binding to multiple receptors with high affinity. In this respect, the therapeutic area that is a subject of intense research is the 5-HT receptors. Pharmacophoric arylpiperazine fragment, which is important structural element in many molecules possessing biological activity, is well recognized by 5-HT_{1A}, 5-HT_{2A}, as well as 5-HT₇ receptors. These serotonin re-uptake inhibitors have emerged as a key mechanics class in the treatment of depression. In our search for a 5-HT selective agonist, we designed and synthesized a series of novel aryl *N*-methylpiperazinyl benzamides.



X = N, C; R = H, Cl

The title compounds were prepared by the reaction of the corresponding aryl piperazine with (benzamidomethyl)triethylammonium chloride in the presence of a small quantity of triethylamine (pH > 9). All these reactions of benzamidomethylation were conducted at room temperature in environmentally friendly aqueous solution, giving almost pure products with high yield.

The structures of the newly synthesized compounds were confirmed by NMR (¹H, ¹³C, DEPT, HMQC), IR, and mass spectral analyses. For further reference of these compounds, antidepressant and psychomotor stimulating activity i.e. behavioral effects of animal models (i.e. rats, mice) after treatment with drug candidates will be evaluated.

Keywords: arylpiperazine, benzamides, serotonin 5-HT receptor agonist

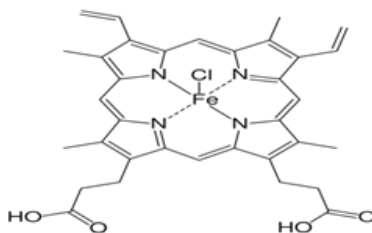
ELECTROCATALYTIC REDOX REACTIONS OF HEMIN MODIFIED GRAPHITE ELECTRODES

Natalija Atanasovska¹, Ionel Catalin Popescu², Graziela Turdean²,
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The redox chemistry of adsorbed hemin on the surface of a graphite electrode was investigated by applying cyclic and square-wave voltammetry. Hemin was immobilized on the graphite electrode by a casting method from a 96% (v/v) ethanol solution. The hemin modified electrode was immersed into potassium chloride electrolyte solution containing phosphate buffers at different pH values. The adsorbed hemin undergoes one-electron reversible electrode reaction due to Fe(II)/Fe(III) redox couple. In the presence of H₂O₂ in the aqueous solution a well defined electrocatalytic effect was observed, in which H₂O₂ was reduced to produce H₂O, facilitated by the adsorbed hemin.



Molecular structure of hemin

Keywords: Electrocatalysis, Voltammetry, Hemin, Hydrogen peroxide



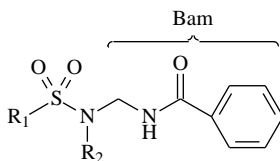
Workshop "From Molecules to Functionalised Materials" – Skopje, March 2011

SYNTHESIS OF SOME NEW *N*-[(BENZOYLAMINO)METHYL]SULFONAMIDES WITH POTENTIAL ANTIBACTERIAL ACTIVITY

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In view of wide spread resistant strains of microorganism there is an urgent need for the development for new therapies in bacterial infection to overcome resistance and to treat these conditions in new ways. Sulfonamide derivatives represent a class of compounds which having interesting pharmacological activities. Many representatives of this class of compounds were reported to have antibacterial activity. Moreover, the promising benefit of the benzamidomethyl derivatives as biological active products and their implication for pro-drug design has been previously reported. These observations have encouraged us to couple these two bioactive fragments hoping to obtain new compound with potential biological activity. In the present communication, the syntheses of novel *N*-[(benzoylamino)methyl]sulfonamides are reported.



R₁ = Ts, Ms; **R₂** = H, Ph, Me, Bam

Further investigations are in progress aimed at examining the above compounds as concerns their activity as antimicrobial agents

Keywords: sulfonamides, benzamidomethylation

STUDYING THE INFLUENCE OF SACCHARIN ON ION TRANSFER PROCESSES ACROSS L|L INTERFACE BY MEANS OF SQUARE-WAVE VOLTAMMETRY

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The simple configuration of three-phase electrode in combination with square-wave voltammetry is a powerful tool for studying the ion transfer processes across an interface between two immiscible liquids. The three-phase electrode is a simplified model for understanding the ion transfer processes across cellular membranes. Using thin organic film modified electrode (i.e., a three-phase electrode) consisting of edge plane pyrolytic graphite electrode (EPGE) partly covered with a microfilm of the organic solvent (nitrobenzene) containing neutral redox probe, lutetium bis(tetra-*tert*-butylphthalocyaninato), LBPC, immersed in an aqueous electrolyte solution (AQ), the transfer thermodynamics and kinetics of the strongly hydrophilic cations Li^+ , Na^+ and K^+ are analyzed in details, in the presence of saccharin in the aqueous phase. From the recorded data, it has been concluded that saccharin facilitates and accelerates the alkali cations transfer across the AQ|NB interface. The transfer of the saccharinate anion has been also studied in a separate experiment and the standard Gibbs energy of the transfer has been determined. Because of a daily usage of the saccharin, the most widely used artificial sweetening agent, studying the complex metal saccharinate ion transfers is necessary, especially of the saccharinate complexes of biologically relevant trace metals, which is the future objective of our work.

Keywords: Square-wave voltammetry, three-phase electrodes, immiscible liquid phases, ion transfer thermodynamics, ion transfer kinetics, saccharin, metal saccharinate complexes



SIMPLE ELECTROCHEMICAL METODOLOGY FOR DEPOSITION OF GOLD NANOPARTICLES USING VOLTAMMETRIC TECHNIQUES BY MEANS OF THIN FILM ELECTRODES

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Simple electrochemical methodology has been developed for deposition of gold nanoparticles on the interface between two immiscible liquid phases, i.e., an aqueous phase (aq) containing $[\text{AuCl}_4]^-$ (aq) ions and an organic phase consisting of a nitrobenzene (nb) solution of decamethylferrocene (DMFC(nb)). The surface of a black graphite electrode was modified with a thin film of the organic phase and the modified electrode was immersed into the aqueous phase. Besides the reversible electrode oxidation of DMFC(nb) at the electrode|nitrobenzene interface, in parallel a spontaneous heterogeneous redox reaction occurs at the nb|aq interface. The latter process includes oxidation of DMFC(nb) to $\text{DMFC}^+(\text{nb})$ in the organic phase and reduction of $[\text{AuCl}_4]^-$ (aq) to Au(s) in the aqueous phase. As the $\text{DMFC}^+(\text{nb})$ can be electrochemically regenerated to DMFC(nb) at the electrode surface by controlling the electrode potential, the DMFC(nb)/ $\text{DMFC}^+(\text{nb})$ plays a role of a redox mediator, shuttling electrons from the electrode to the liquid|liquid interface, resulting in electrochemical deposition of gold particles at the liquid interface. The gold particles on the nb|aq interface were observed by optical microscopy. It was found that the particles are of a nano scale size.

Keywords: Electrochemical deposition; Gold nanoparticles; Thin film electrodes

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- [2] Valentin Mirčeski, Rubin Gulaboski, *Journal of Physical Chemistry* Vol. 110, No 6, 2812-2820, (2006)



LIQUID|LIQUID ELECTROCHEMISTRY OF DECAMETHYLFERROCENE (DMFC) STUDIED BY MEANS OF MODIFIED THIN ORGANIC FILM ELECTRODES. EFFECT OF BLOCKING THE LIQUID|LIQUID INTERFACE BY ELECTROCHEMICALLY DEPOSITED COPPER NANOPARTICLES

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A study of the liquid|liquid electrochemistry of decamethylferrocene (DMFC) by means of thin organic film modified graphite electrodes is presented. Black graphite electrode is modified with a thin film of nitrobenzene solution (NB), containing dissolved decamethylferrocene (DMFC) and $(\text{Bu})_4\text{NClO}_4$ as an organic electrolyte. The modified electrode is immersed into an aqueous electrolyte solution, containing perchlorate ions (ClO_4^-). Heterogeneous electrode oxidation reaction of DMFC occurs, giving raise to a stable and reversible voltammetric response. The redox activity of $\text{DMFC}_{(\text{NB})}$ (i.e., $\text{DMFC}/\text{DMFC}^+$ redox couple) is accompanied by the transfer of anions (ClO_4^-) across the aqueous electrolyte | organic solution interface. In order to study the influence of the transferring anions on the overall electrochemical reaction, the liquid interface was modified by *ex situ* deposited copper nanoparticles. Following the copper deposition, a strong decrease of the voltammetric response of DMFC was observed, due to blocking of the liquid|liquid interface by metal nanoparticles.

Keywords: Liquid|Liquid electrochemistry, Thin film electrode, Electrochemical deposition

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SYNTHESIS OF POLYCARBOXYLIC ACIDS AS ORGANIC LINKERS FOR METAL-ORGANIC FRAMEWORKS (MOFs)

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Metal-organic frameworks (MOFs) are crystalline materials consisting of a metal ion and an organic ligand. The organic linkers should contain at least two carboxylic groups in order to bind to metal ions. The choice of the metal ion and the organic linker is very important as they determinate the properties of the MOFs. MOFs can be used for catalysis, hydrogen storage, gas sorption, etc.

Our goal was the synthesis of triphenylamine-based indoline dyes^{2,3} (Figure 1), as organic linkers for photoactive MOFs.

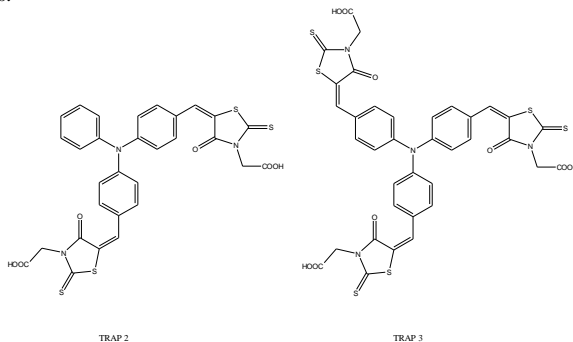


Figure 1. Triphenylamine (TPA)-based dyes

The TPA group, as basic electron donor unit, and the rhodanine-3-acetic acid, as electron acceptor, are the main components for designing this kind of ligands.²

Keywords: Metal-organic framework, dyes

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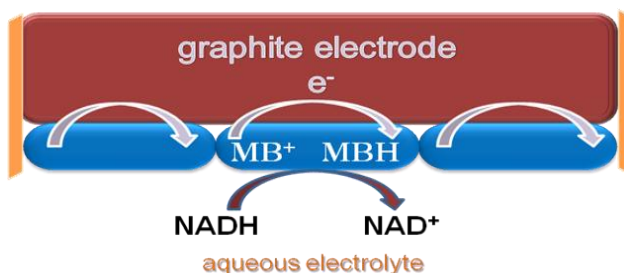
ELECTROCATALYTIC OXIDATION OF NADH WITH MELDOLA BLUE CHEMICALLY MODIFIED GRAPHITE ELECTRODES

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A study of the electrocatalytic oxidation of reduced NADH on a chemically modified electrode with Meldola Blue (MB) is reported. Melodola Blue is a derivate of 3,7-diaminophenoxazine, which can be firmly absorbed on graphite electrode surface to produce a chemically modified electrode. Modification of the electrode is carried out by simple immersing of the bare electrode in a 0.25 mmol/L MB solution for 10 min., followed by drying of the electrode at room temperature for 30 min. The modified electrode was electrochemically investigate applying cyclic and square-wave voltammetry in a phosphate buffer at pH 7 that additionally contained 0.1 mol/L KCl, as a supporting electrolyte. NADH was successfully catalytically oxidized with the modified electrode in an electrode mechanism in which MeIB plays the role of a redox mediator.



Keywords: Electrocatalysis, Voltammetry, Meldola Blue, NADH



Stabilitätspakt für Südosteuropa
Gefördert durch Deutschland
Stability Pact for South Eastern Europe
Sponsored by Germany

Workshop "From Molecules to Functionalised Materials" – Skopje, March 2011

NEW APPROACHES IN USING ISOELECTRIC FOCUSING FOR PROTEIN DETERMINATION IN MULTIPLE SCLEROSIS

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Multiple sclerosis is an inflammatory, demyelizing, autoimmune disease of the central nervous system. It is characterized by multiple symptoms, that often progress and cause severe disabilities in motor neurons.

Isoelectric focusing was used to examine intrathecally synthesized proteins in CSF. The most important protein fraction analyzed is gama globulin, and especially immunoglobulin G (IgG). Also, isoelectric focusing enabled detection of oligoclonal IgG bands in the CSF in patients with multiple sclerosis. These oligoclonal bands served as evidence for the intrathecal, humoral, immunological response. In the process of diagnosing this disease, a comparative analysis of serum and CSF was done. The absence of oligoclonal IgG bands in serum and their presence in cerebrospinal fluid differentiates multiple sclerosis from other neurological disorders with similar CSF findings.

The new approach, we would try to adapt to existing isoelectric focusing is to optimize a method for protein analysis using tears as biological fluid. Using this media, we would be able to contribute to differential diagnosis of multiple sclerosis, using less invasive methods.

Keywords: electrophoresis, isoelectric focusing, multiple sclerosis, oligoclonal bands.



DETERMINATION OF PROTEIN PROFILE ASSOCIATED WITH GUILLAIN-BARRE SYNDROME

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Acute inflammatory demyelinating polyneuropathy or [Guillain-Barré syndrome](#) is an autoimmune disease, which is characterized by progressive, symmetric and ascending muscle weakness. It occurs a few days or weeks after the patient has had symptoms of a respiratory or gastrointestinal viral infection. Produced antibodies trigger abnormal immune response that causes demyelination of peripheral nerves. As a consequence, changes in blood–brain barrier occur, therefore additionally changing cerebrospinal fluid protein concentrations.

For analyzing proteins in cerebrospinal fluid disk electrophoresis has been used. Using this technique, proteins can be separated from the cerebrospinal fluid as highly concentrated protein bands with bigger resolution. Disk electrophoresis was also used for qualitative protein profiling and for quantitative analysis which provided accurate results for the proteins of interest.

Albumin and immunoglobulin G have been analyzed in order to determine the relation between the syndrome and progress of the disease. Obtained results can be processed using specialized software in order to determine the intrinsic parameters, and obtain additional information for verification of Guillain-Barré syndrome. Further analyses are in progress in order to implement other techniques, and also, develop new relations between the proteins.

Keywords: cerebrospinal fluid, disc electrophoresis, Guillain-Barré syndrome, proteins.



QUANTITATIVE ANALYSIS OF ACETYLSALICYLIC ACID USING DRIFT SPECTROSCOPY

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DRIFT Spectroscopy is a powerful tool for quantitative and qualitative analysis and an excellent alternative for the classic infrared spectroscopy [1]. It can be used in analysis of crystalline powders. The basis for quantitative analysis, using DRIFT, is the validity of the Kubelka-Munk function [1]. The aim of this work is to study the applicability of the DRIFT technique for quantitative analysis of powdered samples. As an investigated material, acetylsalicylic acid was used. The technique depends on several parameters like: particle size, concentration, mirror-like reflection and the sample cup-filling (filling density). The most common way of sample preparation, employing dilution method [1], is through flattening of the sample cups. However, the biggest deviations from linearity appeared to be due to the sample cup-filling that varied from measurement to measurement. This was in direct connection to the filling density of the cups, too. Thus, another approach, as suggested in the literature [2] was employed. Sample cups were filled in a controlled way and further on, the same amount of pressure for each measurement were applied. As a result, much better linearity of the absorption v.s. concentration was achieved, together with RSD approaching analytical limits.

Keywords: Kubelka-Munk theory, powder substances, acetylsalicylic acid, DRIFT

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GAMMA SPECTOMETRY ANALYSIS OF RADIONUCLIDES IN SOILS

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Natural radionuclides in the soil are the main external source of irradiation of the population. Natural environmental radioactivity and associated external exposure due to gamma-radiation depends primarily on the geological and geographical conditions, and appears at different levels of radionuclides in the soil of each region in the world [1]. Concerning the Republic of Macedonia, complete study of the soils in Macedonia has been performed [2].

The external exposure on the human being from terrestrial radiation is directly connected with the concentration of ²²⁶Ra, ²³²Th and ⁴⁰K in the soil. Our research also included determination of the specific activity of soil samples on ¹³⁷Cs, which is an artificial radionuclide formed mainly as a fission product. The mean specific activity of natural radionuclides found in the investigated soil are: (²²⁶Ra) 33.9 ± 15.1 Bq kg⁻¹, (²³²Th) 46.3 ± 22.5 Bq kg⁻¹ and (⁴⁰K) 568.5 ± 262.7 Bq kg⁻¹. These values fall within the worldwide ranges as reported in literature [1]. The highest activity found for ¹³⁷Cs was 56.3 Bq kg⁻¹ (Lakavica).

Continuous monitoring of the radiation is the basic step in caring for a safe and healthy environment.

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RAMAN SPECTROSCOPIC METHOD FOR DETECTION OF TRACES OF RARE EARTH ELEMENTS IN MINERAL SAMPLES

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The rare earth elements (REEs) are an important group of elements poorly represented in chemical education (especially in laboratory experiments), mostly because of their low abundances and the radioactive properties of those minerals where REEs are present as major constituents. Therefore, instead of practical laboratory work with such samples, the recommended and common approach is to use minerals incorporating traces of REEs. In this way, the important features of the abundance and geochemistry of the REEs could be easily demonstrated if simple laboratory experiments are designed. Here, we propose a convenient and efficient Raman spectroscopic method for detection of traces of REEs in minerals on the basis of the appearance of corresponding laser-induced luminescence bands. Namely, the observed Raman fluorescence, registered solely by near-infrared laser excitation, is explained by the energy similarity of the REEs atomic energy levels splitting caused by the influence of the mineral host [1]. The method is exemplified using the Raman spectra of almandine and spessartine mineral samples (see Figure), the former and the later being with and without traces of REEs, respectively [2].

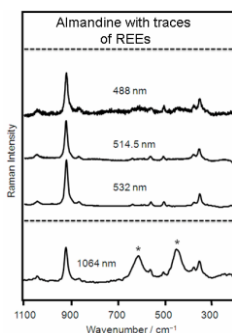


Figure. Raman spectra of almandine obtained by visible (488, 514.5, 532 nm) and near-infrared (1064 nm) excitation. Bands in the last spectrum marked by asterisks are laser-induced fluorescence bands.

Keywords: Laboratory experiment, Rear earth elements, Raman spectroscopy, Fluorescence

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SYNTHESIS AND CHARACTERIZATION OF CO (II) COMPLEXES WITH TRIDENTATE (ONO) SCHIFF BASES

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New complexes of cobalt (II) have been prepared in the reaction mixture of cobalt (II) acetate, ethanolamine and 5-X salicylaldehyde (X=Br, Cl) under nitrogen atmosphere. Bis(2-hydroxyethylimino)methyl)-4-bromophenolato) cobalt (II) and Bis(2-hydroxyethylimino)methyl)-4-chlorophenolato)cobalt (II) were characterized by elemental analysis, IR spectroscopy and ESI mass spectrometry. Elemental analysis and mass spectrometry data of the complexes suggests the stoichiometry ratio of 1:2 (metal-ligand).

Keywords: Schiff base, cobalt complexes, IR spectroscopy, mass spectrometry.

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PREPARATION AND CHARACTERIZATION OF POLYMER/LAYERED SILICATE NANOCOMPOSITES

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The field of nanotechnology is one of the most popular areas for current research and development in basically all technical disciplines. This obviously includes polymer science and technology and even in this field the investigations cover a broad range of topics (1). Polymer – clay nanocomposites are hybrid organic inorganic materials, in which mixing of the filler phase is achieved at the nanometer level, so that at least one dimension of the filler phase is less than 100 nm. Among polymer/clay hybrids, iPP-nanocomposites have recently attracted great research interest, owing to a good balance of properties of iPP and wide fields of its application. Clay minerals, due to their unique layered structure, rich intercalation chemistry and availability at low cost, are promising nanoparticle reinforcements for polymers to produce low-cost, lightweight and high performance clay based-polymer nanocomposites (2). Two different techniques for preparation of polypropylene/clay nanocomposites are used: melt mixing and latex technology, which was successfully used for preparation of polypropylene nanocomposites with high dispersion quality (3). WAXD, SEM, TEM, AFM, DSC, POM, TGA and DMTA are used for characterisation of polypropylenes nanoclays and nanocomposites.

Keywords: nanocomposites; polypropylene; clay; characterization

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SYNTHESIS OF SOME NEW AZO DYES DERIVED FROM 4-HYDROXY COUMARIN

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From first discovery (anticoagulant) till today, a very wide spectrum of biological and pharmacological activities of coumarin and its derivatives were confirmed. Most important are the Anti-Hiv [1-2] and anti-cancer [3-4] activities of some of those derivatives. Working in this field some azo coumarin dyes were synthesized by the coupling of 4-hydroxycoumarin and diazonium salts, which obtained by diazotization of aryl *o*-diamines, such as *o*-phenylenediamine or 4-methyl-*o*-phenylenediamine (at -5 °C). These reactions occurred rapidly, giving colourful voluminous precipitate. Those products are very soluble in almost every organic solvent at room temperature, that didn't allow to purify them by simple recrystallization and the purification was made by column chromatography. Those derivatives are with biological potential and are very suitable for use as tetradentat ligands for various metals.

Keywords: synthesis, azo dyes; 4-Hydroxy coumarin; aryl *o*-diamines.

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NEW COMPLEXES OF NICKEL (II) AND COBALT (II) WITH 4-HYDROXY-2-OXO-2H-CHROMENE-3-CARBOXAMIDE

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The reactions of Nickel (II) and Cobalt (II) chloride with 4-hydroxy-2-oxo-2H-chromene-3-carboxamide as ligand (HL) in the mixture of ethanol-water solution gave polinuclear complexes of types $[M_2L_2Cl_2(H_2O)_4]$, where $M = Ni^{II}$ or Co^{II} . The triethylamine have been used for deprotonation of hydroxyl group of the ligand. New complexes have been characterized on the basis of elemental analyses, IR and mass spectrometry. The results are in accord with an octahedral environment around the M (II) ion.

Keywords: Nickel (II) and Cobalt (II) polinuclear complexes, 4-hydroxycoumarine derivatives, IR spectroscopy, mass spectrometry.

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IDENTIFYING AND ISOLATION OF THE GENE ENCODING CHLOROPLAST SOD IN HABERLEA RHODOPENSIS

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Reactive Oxygen Species (ROs) are products of the metabolism of the aerobic organisms. This group is comprised of several high reactive radicals: the superoxide radical ($\cdot\text{O}_2^-$), hydrogen peroxide (H_2O_2) and hydroxyl radical ($\cdot\text{OH}$) and singlet oxygen (O^1_2).

An increased production of these radicals can be observed due to some stress conditions as intensive light, drought, pathogens or wounding. Their accumulation can cause damage in DNA, changes of the permeability of the cell membrane e.c.t (Fridovich, I.1998)

Several enzymes are employed in maintaining the optimal redox state in the living cells among which is the superoxide dismutase (SOD). It's a group of metal enzymes, which catalyze the transformation of O_2^- to H_2O_2 , by process of oxidation and reduction of the metal cofactor. (Bowler *et al.*, 1994)

Haberlea rhodopensis shows great drought resistance. The analysis of the activity of the SODs in leaves of the plant in the process of dehydration and rehydration shows increased SOD activity compared with other plant species.

In recent studies several SOD isoforms were isolated and their sequences are annotated in NCBI (Denev *et al.*), but still one of the major isoforms the Cu/Zn-SOD is still not isolated. The aim of this study is to design primers and optimize the PCR conditions in order to isolate the gene or a fragment of the gene which encodes this isoform.

Degenerative primers were used for amplification of the nucleus encoded, chloroplast localized Cu/Zn-SOD. The PCR products were isolated, purified and cloned in pDrive vector and transformation of *E.coli* was performed. The positive colonies were isolated, and the purified plasmids were sequenced. The results showed that the isolated sequence is a part of exon from the gene for Cu/Zn-SOD. This will help in designing gene specific primers for the gene of Cu/Zn-SOD.

Keywords: superoxide dismutase, reactive oxygen species, *Haberlea rhodopensis*

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CRYSTAL ENGINEERING OF PHARMACEUTICAL COCRYSTALS

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Cocrystals have recently gained attention as attractive alternate solid forms for drug development. A pharmaceutical cocrystal is a single crystalline homogenous phase consisting of a drug molecule and ligand i.e. cocrystal former that is excipient or another drug molecule [1,2]. The different components in the cocrystal are neutral in nature when compared to salts that have ionized components. [1,2,3]. The components in a cocrystal exist in a definite stoichiometric ratio, and assemble via non-covalent interactions such as hydrogen bonds, ionic bonds, π - π or van der Waals interactions. Cocrystals thus possess different composition and structure when compared to the crystals of parent components.

Examples in the preceding section show that cocrystallization alters the molecular interactions and composition of pharmaceutical materials. As such one can expect changes in physico-chemical properties such as chemical stability [4], hygroscopicity [5], dissolution rates and solubility [6] compressibility [6] due to cocrystallization of pharmaceutical materials.

To formulate Pharmaceutical Cocrystal(s) will be used two drugs which proton-acceptor and/ or proton-donor functional groups can form syntons toward H-bonding with appropriate to them functional group encompassed in their structure. The selection of drug models will be done according to their performance of dual or complementary pharmacological responds in therapy. The formulated cocrystal of two drug molecules will present New Chemical Entity (NCE) that offer opportunity to be cover with patent protection and further to be used as single Active Pharmaceutical ingredient in combo i.e. fixed pharmaceutical formulation that perform dual action in therapy.

Research methodology encompasses the drug cocrystal screening toward applying procedures for crystallization, and analytical techniques for characterization of formed cocrystal in solid state and in solution, respectively.

Keywords: drug cocrystals, crystallization, solid state characterization

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POLYPHENOLIC PROFILE AND RESULTING ANTIOXIDANT ACTIVITY OF MACEDONIAN WINES AND BY-PRODUCTS

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The content of *trans*-resveratrol and its glucoside piceid as major stilbenes in wines and the relationship between their content and winemaking technology has been studied in Macedonian red wines from the two main grape varieties Vranec and Merlot. Moreover, the effect of winemaking technology including time of maceration, type of yeast and the level of sulfur dioxide applied on the stilbenes content and antioxidant activity of the wines has been studied. The results imply that the most important factor in winemaking technology affecting the stilbenes content and antioxidant activity is the maceration time since the highest concentrations of *trans*-resveratrol and piceid were found in red wines from both varieties produced with 6 and 10 days of maceration [1]. Concerning the yeast type, higher concentration of *trans*-resveratrol and piceid as well as higher antioxidant activity have been obtained with French yeast in comparison to Macedonian yeast. Higher concentration of SO₂ protects the phenolic compounds in wines from oxidation during the winemaking process but, it does not affect significantly the concentration of both analyzed stilbenes in wines.

Isolation of anthocyanins as high valuable antioxidants from three red varieties (Vranec, Merlot and Pinot Noir) of grape pomace by application of countercurrent chromatography was also performed. After purification of the fractions by means of preparative high performance liquid chromatography the structures of isolated pigments were elucidated by electrospray ionization multiple mass spectrometry and nuclear magnetic resonance (NMR) spectroscopy. The major anthocyanin was malvidin-3-glucoside and also delphinidin-3-glucoside, cyaniding-3-glucoside, petunidin-3-glucoside, peonidin-3-glucoside and malvidin-3-p-coumaryl-glucoside were isolated. "Color activity concept" and visual detection thresholds of isolated anthocyanins were applied and the results were in good agreement with the color of the different varieties of red grape pomace.

Keywords: red wines, wine-making technology, maceration time, yeasts, SO₂, CCC, HPLC-MS, HPLC-DAD, polyphenols, anthocyanins, stilbenes, antioxidant activity, ABTS.

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THE SYNTHESIS OF NEW PHENOTHIAZINYL PORPHYRINS AND THEIR METAL(II) COMPLEXES

Brem Balazs

Reaction of pyrrole and an aromatic aldehyde at room temperature affords the corresponding tetraarylporphyrin in high yield.

Phenothiazine and phenyl substituted derivatives of the porphyrin have been prepared. The derivative of porphyrin which contains one phenothiazine group was obtained by acid catalyzed condensation of 10-methyl-3-formyl-phenothiazine, pyrrole and benzaldehyde followed by oxidation with p-chloranil. Formylation of the 10-methyl-phenothiazine ring at position 3 was achieved via Vilsmeier-Haack reaction.

5-phenyl-2,2'-dipyrromethane was obtained by electrophilic substitution of pyrrole with benzaldehyde in acid catalyst and then subjected to the reaction with 10-methyl-3-formyl-phenothiazine in stoichiometric amount, thus generating a bis-phenothiazinyl-porphyrin derivatives.

Phenyl-Phenothiazinyl-Porphyrins were complexed with divalent metal acetates (Cu, Ni, Co). The structures of the new compounds were assigned based on: MS, ¹H-NMR, ¹³C-NMR, UV-Vis, FL spectra.

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BIENZYMATIC AMPEROMETRIC BIOSENSOR FOR GLUCOSE DETECTION IN WINE

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An amperometric biosensor for glucose detection was developed and successfully applied for glucose monitoring in wines. The bienzymatic biosensor was obtained by immobilization of glucose oxidase (GOx), horseradish peroxidase (HRP) and Os(II)-redox hydrogel on a graphite electrode, by using poly(ethylene glycol) diglycidyl ether (PEGDGE).

Using cyclic voltammetry, the investigated bielectrode showed a quasi-reversible electrochemical redox behavior with a formal potential of 50 mV (vs Ag/AgCl, KCl_{sat}), characteristic for Os(II)/Os(III) couple (0.1 M phosphate buffer; pH 6.74; 25 °C). The influence of experimental conditions, such as pH solution and the scan rate potential were investigated in order to attain the optimum analytical performances.

The immobilized mediator Os(II)-redox hydrogel displayed an excellent electrocatalytic activity for the H₂O₂ reduction.

The analytical parameters for H₂O₂ and glucose amperometry detection were: linear range up to 1 mM for glucose and up to 0.3 mM for H₂O₂; sensitivity 1.29 ± 0.03 μA/mM for glucose and 29.17 ± 2.55 μA/mM for H₂O₂; detection limit of 0.003 mM for glucose and 0.006 mM for H₂O₂; response time t_{95%}, 20 s for glucose and 10 s.

Using the Michaelis–Menten formalism, the kinetic parameters were found as follows: Michaelis–Menten constant, K_M, 2.25 ± 0.20 mM for glucose and 0.21 ± 0.02 mM for H₂O₂.

The results obtained for real samples wines were found in good agreement with those reported by the vineyard.

Keywords: amperometric biosensors; glucose oxidase; horseradish peroxidase; wine; glucose.

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HEMOGLOBIN-ALBUMIN CROSSLINKED COPOLYMERS: REDUCED PROOXIDANT REACTIVITY

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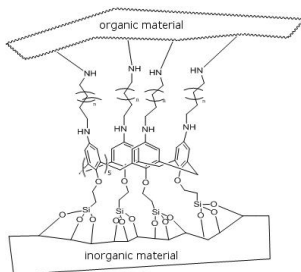
We have previously reported that derivatization of hemoglobin with periodate-modified sugar derivatives such as oxidized adenosine triphosphate (oATP) leads to an increase in prooxidant reactivity at the heme. Here, we report that copolymerization of hemoglobin with serum albumin alleviates this problem completely, to the extent where the copolymer even has a slightly lower autooxidation rate compared to native hemoglobin. A similar, although not as potent, effect is obtained when hemoglobin is derivatized with oATP in the presence of small-molecule antioxidants instead of albumin.

Keywords: Hemoglobin-based blood substitutes, periodate, albumin, antioxidant.

SUBSTITUTED CALIXARENES - PRECURSORS FOR COMPOSITE MATERIALS

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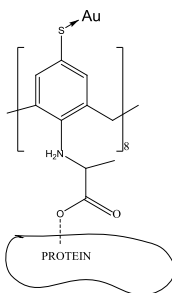
Substituted calixarene can act as interfaces in achieving composite materials. These macrocyclic systems can adhere to both inorganic and organic surfaces when the suitable functional groups. For instance, calix[8]arene substituted with thiolic units at the upper-rim and appropriate organic groups at the lower-rim can be employed as interface in the construction of inorganic/substituted calyx[8]arene/organic materials (Scheme 1)



Scheme 1.

Our group is interested in the synthesis of such frames in which the inorganic substrate consists of metallic nanoparticles (eg: Au, Ag) and the organic moiety can be represented by a proteic fragment from a biologic tissue.

A substituted calixarene that can be used for these type of systems is thoroughly described in Scheme 2.



Scheme 2.



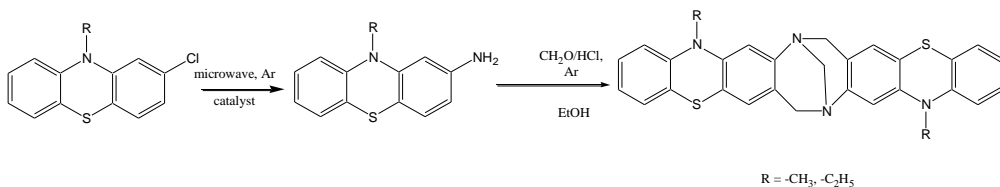
SYNTHESIS AND CHARACTERIZATION OF NOVEL TRÖGER'S BASES WITH PHENOTHIAZINE UNITS

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Tröger's bases are a group of substances that have recently reemerged in research because of their unique properties as chiral agents, receptors or catalyst. This work shows the synthesis and characterization of novel Tröger's bases with phenothiazine units starting from cloro-phenothiazines with an amino-phenothiazine intermediate. The reaction conditions and synthesis of two such Tröger's bases (6H, 2H-tetrahydro-10''Me, 10''Me-2,3-phenothiazinyl-[1,5]diazocine, and its ethyl correspondent) are discussed and characterization of the molecule is done with ¹H-NMR, ¹³C-NMR, UV-Vis and fluorescence spectroscopy. We undertook a series of reaction conditions to reveal the best synthetic route. Physical characterization methods reveal properties that could be valuable in further research.



Keywords: Tröger's base, phenothiazine, molecular symmetry, chiral.

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FORMATION OF COMPOSITE FILM THROUGH REDUCTION OF 2,6-DIMETHYLBENZENEDIAZONIUM IN ACETONITRILE

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The electroreduction of aryldiazonium salts is a very powerful method for surface modification¹. One can obtain covalently attached organic layers with different thickness. The steric hindrance can be used as appropriate way to control film growth. When the 2,6-dimethylbenzenediazonium (2,6-DMBD) is electrochemically reduced, the two dimethyl groups prevents the attachment of this radical onto surface², instead, when produced in greater amounts they can abstract a hydrogen atom from acetonitrile (solvent) thus forming a cyanomethyl radical³ ($\cdot\text{CH}_2\text{CN}$) that binds to the surface. By reduction of 2,6-dimethylbenzenediazonium in acetonitrile (ACN) surfaces of copper, silicon and gold are modified covalently by organic film containing amino groups⁴.

The characterization of the formed films is done by infrared absorption reflection spectroscopy (IRRAS), scanning electron microscopy (SEM), time of flight secondary ion spectroscopy (ToF-SIMS), ellipsometry, water contact angles and cyclic voltammetry.

Keywords: 2,6-dimethylbenzenediazonium, surface modification, acetonitrile, hydrogen abstraction.

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INTERACTION OF Cd(II) IONS WITH SUCCINIC ACID

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This experimental research shows the complexation and precipitation of Cd (II) ions with succinic acid in two different pH (pH=6 and pH=4). The experimental measures in liquid state are determined with polarograph. During our experimental work we have noticed that Cd(II) ions with succinic acid in both pH values show well defined polarographic waves. According to experimental results shown in this research we can conclude that succinates play a huge role in the formation of Cd(II)NTA complex, especially in solutions with pH=4 in which Cd(II) ions form labile Cd(II) succinate complex.

To complex Cd(II)ions to perchlorates it is necessary almost equivalent quantity of NTA, while in succinate solutions to achieve the same level of complex we need a much bigger amount of NTA, because the labile complexes of Cd(II) interfere with stabile complex of Cd(II)NTA.

The precipitation of Cd(II) ions with succinic acid has been researched in concentration of Cd(II) ions from $C=4 \cdot 10^{-3}$ to $1.5 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ and the concentration of ligand has been $C=0.1, 0.2, 0.3$ and $0.4 \text{ mol} \cdot \text{dm}^{-3}$. As the concentration of ligand was grown, we noticed the dissolution of precipitates because the soluble Cd(II) ligands are formed.

From the solid state the specter IR was detected and compared to the IR specter of ligand and was observed the significant difference in both the forms and in intensity of the spectral lines.

Keywords: cadmium(II), complexation, ligands, precipitation, labile complexes.

HIERARCHICALLY STRUCTURED SILICA VIA COMBINATION OF SALT SINTERING PROCESS AND PHASE SEPARATION

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Hierarchically structured, porous materials are desirable for their increased permeabilities and low pressure drops coupled with high surface areas. Recently an enormous research has been focused on the synthesis and applications of such materials. In this study we demonstrate the preparation of hierarchically structured silica which combines the properties of sintered glasses and porous VYCOR-glasses [1].

Open-pored monoliths were produced by pressing and sintering a mixture of sodium borosilicate glass and an inorganic salt as filling material. Pore sizes and porosity can be adjusted by grain size and volume fraction [2]. An interconnected pore structure was obtained by removing the salt with water after sintering. An additional pore system inside the walls of the sintered material was obtained via a thermally induced phase separation. The leaching of the sodium-rich borate phase finally led to hierarchically organized, porous silica [3].



Fig. 1: Flexible geometric shapes of sintered glasses: Tubes, rods, granules and plates were successfully prepared.

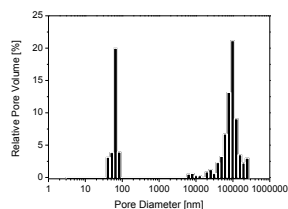


Fig. 2: Pore size distribution of hierarchically structured silica monolith. Primary and secondary pore sizes can be adjusted independently.

The monoliths exhibit specific surface areas up to 420 m²/g and specific pore volumes up to 1.3 cm³/g. Hierarchically organized silica monoliths with very flexible macroscopic shape (Fig. 1) and secondary pores in the range between 50 and greater than 1000 μm can be prepared. The size of the pores inside the silica walls can be independently adjusted in the range between 1 and 500 nm (Fig. 2).

Keywords: glass, hierarchical, porous, shaping, sintering

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POROUS SILICA MEMBRANES AS COMPONENTS OF BIOSENSORS

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Porous silica membranes with monomodal and bimodal pore structures were tested for sensor applications [1]. Porous VYCOR glass and hierarchical sol-gel materials were used as membranes. The sol-gel membranes were obtained by a modified sol-gel process whereupon a secondary macropore system (bimodal pore structure) was created via a polymer induced phase separation. Mesopores with diameters in a range between 6 and 50 nm were generated via hydrothermal treatment with ammonium hydroxide solution.

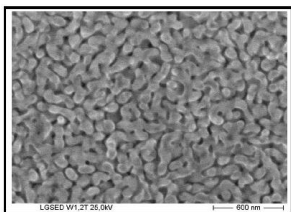


Fig. 1: electron microscopic picture of the monomodal pore structure of a porous glass membrane

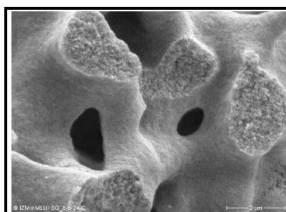


Fig. 2: electron microscopic picture of the bimodal pore structure of a sol-gel membrane

The surface of the membranes was functionalized with different silane coupling agents to immobilize the enzyme Acetylcholinesterase for sensor application [2, 3]. The hydrolysis of Acetylcholinchloride was used as test reaction. Acetic acid was formed as byproduct. This led to a decrease of the pH-value in the solution. Pesticides reduce the activity of the immobilized enzyme and therefore the detection of the pesticides Carbofuran and Metamidophos was possible. In comparison with porous glass membranes with monomodal pore structure the sol-gel materials with a bimodal pore system showed a faster response time.

Keywords: sol-gel, hierarchical, acetylcholinesterase, biosensor

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Stabilitätspakt für Südosteuropa
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Workshop "From Molecules to Functionalised Materials" – Skopje, March 2011

MOLECULAR PRECURSORS FOR CHIRAL PHOSPHORUS-BASED METAL-ORGANIC FRAMEWORKS

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Metal-organic-frameworks (MOFs) have potential use in chemistry as solid, crystalline materials which are derived from organic molecules (linkers) and metal-containing units, so-called secondary building units (SBUs). These materials can find applications in storage of various gases (most importantly hydrogen) with a potentially higher capacity than active carbon or zeolites. Furthermore, MOFs could also be used for drug delivery for a slow release in small doses. Another use would be cleaning and separation of mixtures of gases or liquids, or as materials with unusual properties (optical or magnetic properties, conductivity).

Last but not least, and this is my research focus, MOFs could provide a suitable environment for catalytic reactions. Thus, typical homogeneous catalysts will be immobilised in the three-dimensional framework facilitating easy separation and reuse. The MOF's porosity will be used as a possible way to introduce substrate size selectivity, moreover providing a reaction chamber that mimics the active site of an enzyme – resulting in a unification of aspects of homogeneous and heterogeneous catalysis with an inspiration from nature's enzymes.

This target is addressed by creating suitable tri- or higher-functionalized linkers, having the necessary functional groups to coordinate to nodes and providing a second functional group suitable for coordinating to a catalytically active metal, such as Rh, Pd, Pt or others.

The presentation will give an overview on MOFs as well as some results of my research.

Keywords: Metal organic frameworks (MOFs), homogeneous, heterogeneous catalysis, gas storage, coordination polymers

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OPTIMIZATION OF EXTRACTION METHOD OF PHENOLIC COMPOUNDS AND FREE RADICAL SCAVENGING POTENTIAL OF BLACKBERRY (*RUBUS FRUCTICOSUS*) FRUIT EXTRACT

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Several studies suggest that some phenolic compounds ingested in high concentrations may show positive roles in carcinogenicity, genotoxicity, thyroid toxicity, and estrogenic activity. Extraction of fruit is one of the important factors affecting the concentration of phenolic compounds in fruit extracts. Extraction method that more exploiting the concentration of polyphenols will increase antioxidant capacity and physiologic effects of fruit extracts. Our work was focused on the optimization of extraction method and the spectrophotometric determination of the phenolic composition of blackberry (*Rubus fruticosus*) fruit extract. The effect of different solvent systems and extraction time on the yield of extracted polyphenols from fruit was investigated. In aqueous extract the yield of polyphenols decreased, whereas in methanolic and ethanolic extracts their content increased with the time of extraction. The free radical scavenging potential of this fruit extract was determined using DPPH assay. All investigated extracts are showed significant antioxidant activity and high degree of correlation with the polyphenol content.

Keywords: blackberry, extraction methods, phenolic composition, DPPH scavenging assay.

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Stabilitätspakt für Südosteuropa
Gefördert durch Deutschland
Stability Pact for South Eastern Europe
Sponsored by Germany

Workshop "From Molecules to Functionalised Materials" – Skopje, March 2011

HPLC ANALYSIS OF SOME PHENOLIC COMPOUNDS IN CABERNET SAUVIGNON WINES

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Wines contain a number of biologically active compounds and are subject of continual interest due to their beneficial effects on human health. The health protective properties of wines are associated with their antioxidant activity. Phenolic composition of grape and wine, determined by the relative proportions of the different phenolic compounds, are characteristic for each grape variety and wine, corresponding. The aim of this study was to determine the concentration of some phenolic and hydroxycinnamoyltartaric acids, flavan-3-ols and flavonols, produced of Cabernet Sauvignon wines from different vineyard regions in Serbia. These compounds are analyzed by high-performance liquid chromatographic (HPLC) method with photodiode array and fluorescence detection.

Keywords: Cabernet Sauvignon wines, phenolic compounds, HPLC analysis.

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DETERMINATION OF TOTAL PHENOL CONTENT AND ANTIMICROBIAL ACTIVITY OF TOMATO (*LYCOPERSICON LYCOPERSICUM L.*) EXTRACT

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Tomato (*Lycopersicon lycopersicum L.*) is not only nutritious and dietetic product, but it is also has a wider significance for the organism as prophylactic. The object of the paper has been to examine possible correlations between the total phenol content and antimicrobial activity of tomato ethanol extract. The content of total phenols has been determined by means of the Folin-Ciocalteu spectrophotometric method. The antimicrobial activity has been determined by the disc-diffusion method for the strains of *Staphylococcus aureus* ATCC 25923, *Salmonella enteritidis (D)* ATCC 13076 and *Escherichia coli* ATCC[®] 25922. Tomato extract has produced a similar antibacterial effect on *S. enteritidis* and *S. aureus*, the inhibition zone diameter is 28 mm and 27 mm, corresponding. A lower inhibitory effect (24 mm) towards *E. coli* has been produced. The inhibition zone diameters have been compared with the reference antibiotic chloramphenicol and their value is 23 mm for *Staphylococcus aureus* and *Escherichia coli*, and 27 mm for *Salmonella enteritidis*.

Keywords: tomato extract, total phenols, antimicrobial activity.

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A RAPID SPECTROPHOTOMETRIC METHOD FOR DETERMINATION OF RESORCINOL CONTENT

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Resorcinol (benzene-1,3-diol) is used as a chemical intermediate for the synthesis of different pharmaceuticals and other organic compounds (resorcinarene macrocycle molecules, diazo dyes, UV absorbers, plasticizers). Resorcinol reacts with formaldehyde to form a thermoset resin, which can form the basis of an aerogel. It is used 5 to 10% in ointments in the treatment of chronic skin diseases such as psoriasis and eczema a sub-acute as an antiseptic and disinfectant. Resorcinol can be included as an anti-dandruff agent in shampoo, medicated soaps or in sunscreen cosmetics. A rapid and low-cost spectrophotometric method for determination of resorcinol content involve addition of a known excess of bromate to resorcinol solution in an acid medium, followed by determination of residual bromine and chlorine reacting with methyl orange and measurement of absorbance at 505 nm. The absorbance increases linearly with resorcinol concentration (correlation coefficient is 0.9998).

Keywords: resorcinol content, spectrophotometric method, medicinal formulations.

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DETERMINATION OF UV-EFFECT ON ANTIOXIDANT ACTIVITY OF VRANAC GRAPE EXTRACT

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In recent decades, polyphenolic compounds cause great interest because of their chemical impact on the quality of food and their biological activity as antioxidants, antitumoral, antiallergenic and positive impact on coronary heart disease. In this work the effects of ultraviolet radiation (UV) on the antioxidant action of polyphenols in the extracts of Vranac grape were studied by the DPPH (1,1-diphenyl-2-picrylhydrazyl) assay. This method is based on the measurement of the decrease of the free DPPH radical absorbance at 517 nm caused by the antioxidant action of polyphenol compounds, which appeared to be strongly affected by UV-action. The high-energy input of the involved UV-photons plays a major governing role. Antioxidant activity of grape extracts appeared to be most resistant to UV radiation which is in agreement with found higher polyphenol content in grape extract.

Key words: UV radiation, Vranac grape, polyphenol content, antioxidant activity.

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DETERMINATION OF PHENOL CONTENT AND ANTIOXIDANT ACTIVITY OF LEEK (*ALLIUM PORRUM L.*) EXTRACT

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Phenolic compounds exhibiting antioxidant properties are an important component contributing to the beneficial effect of fruits and vegetables on human health [1-3]. Their ability to affect diseases resulting from oxidative stress has not been sufficiently elucidated. This study was aimed at evaluating the antioxidant activity and phenol content of leek (*Allium porrum L.*) ethanolic extract. Total phenols were determined using the modified Folin-Ciocalteu spectrophotometric method. Antioxidant activity was assessed by scavenging the stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH). The results on antioxidant activity were compared with control antioxidants: vitamin C and BHT.

Keywords: Leek extract, total phenol content, antioxidant activity, DPPH assay.

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GRAPE WASTE AS ALTERNATIVE SOURCE OF NUTRITIONAL ANTIOXIDANTS

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Grape growing contributes to the Serbian economy in diverse ways. The grape products are rich sources of health-promoting polyphenols. These compounds have been of great interest to the food industry due to their benefits as anti-aging, anti-carcinogenic, anti-mutagenic, anti-microbial and antioxidant effect. During winemaking, large quantities of grape waste is produced. In the Serbia, the grape industry was produced 431 000 tons of grapes in 2009. From this, an estimated near 200 000 tons grape waste. This grape by-product has been investigated previously as a potential feed for livestock and as an organic fertilizer. The our results of analysis of Cabernet Sauvignon grape extracts show high contents of total phenols reflecting their high antioxidant activities (from 85.40 ± 0.76 to $99.42 \pm 0.56\%$). The grape by-products, constitute a very cheap source for the extraction of antioxidants, which can be an alternative source for obtaining nutritional antioxidants (dietary supplements), thus providing an important economic advantages.

Keywords: grape waste, nutritial antioxidant, economic potential.

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