



**БЕСТИ – NEWS**

## IN MEMORIAM

**ПАНЧЕ КИРКОВ**  
1927–2007

На 30 април о.г. почина д-р. Панче Кирков, редовен професор во пензија и еден од основачите на Технолошко-металуршкиот факултет во Скопје.

Проф. Панче Кирков бил роден и завршил гимназија во Велес. Хемиска технологија дипломирал на Сеучилиштето во Загреб, во 1952 година. Докторирал (електрохемија) на истото Сеучилиште во 1956 година. Предавал хемија на Медицинскиот факултет во Скопје, а од 1961 година, па до пензионирањето во 1987 година работел на Технолошко-металуршкиот факултет во Скопје.

Основач е на Заводот за физичка хемија и електрохемија и на лабораториите по повеќе дисциплини. Предаваше физичка хемија, електрохемија, радиохемија, физичка хемија на макромолекули и друго.

Заслужен е за ангажирањето на млади кадри на новоотворениот Технолошко-мета-

луршки факултет. Заслужен е исто така и за создавањето и напредувањето на Центарот за примена на радиоизотопи во стопанството на Република Македонија, за организирањето Меѓународна летна школа по квантна електрохемија и за издавањето на Билтенот на Технолошко-металуршкиот факултет во Скопје (денес претопен во Гласникот на хемичарите и технолозите на Македонија).

Проф. Кирков оствари интензивна меѓународна соработка и долги години беше експерт на Обединетите нации во Египет, Индија, Франција и САД.

Во сеќавањата на колегите од Технолошко-металуршкиот Факултет во Скопје, како и на членовите на Сојузот на хемичарите и технолозите на Македонија проф. Панче Кирков ќе биде запаметен како млад, енергичен и претприемчив човек кој ја создаваше историјата на Факултетот и кога беше и кога не беше негов декан. Тој беше визионер, човек со голема фантазија и ретки квалитети. Ќе го паметиме проф. Кирков по неговите добри дела.

Д-р. Светомир Хаџи Јорданов,  
професор по физичка хемија и  
претседател на Сојузот на хемичарите  
и технолозите на Македонија

**DOCTORAL THESIS**  
**DEFENDED AT THE Sts CYRIL AND METHODIUS UNIVERSITY,**  
**FACULTY OF TECHNOLOGY AND METALLURGY**  
**IN SKOPJE, 2006**

**Vesna Dimova**

**PHYSICAL-CHEMICAL CHARACTERISTICS**  
**OF THE NEWLY SYNTHESIZED 1,2,4-TRIAZOLE**  
**DERIVATIVES**

**A b s t r a c t:** The physical-chemical characteristics of a series of substituted 1,2,4-triazole derivatives, were investigated by UV-VIS spectroscopic method. The following substances were selected:

- 4,5-disubstituted-2,4-dihydro-3H-1,2,4-triazole-3-thiones (series I),
- N1-arylaminomethyl/ethyl-1,2,4-triazoles (series II),
- N<sup>1</sup>-heteroarylaminomethyl/ethyl -1,2,4 – triazoles (series III) and

– 1,4-disubstituted thiosemikarbazides (series IV).

The electronic absorption spectra of the examined 1,2,4-triazole derivatives have been studied and the position of the characteristic absorption maximums and the type of the electronic transition were defined.

The acid-base equilibrium to a part of the selected compounds was studied by defining the changes of the recorded UV spectra which occur as a result of the reaction of protonation. Protonation constants were calculated using two methods: *HAFM* and *EAFM*. The dissociation of selected triazole derivatives was investigated following the changes in the electronic absorption spectra of aqueous solutions of the investigated compounds in NaOH. Dissociation constants were calculated within water solutions of NaOH with different pH.

The UV spectra of 1,2,4-triazole derivatives were recorded in protic and aprotic solvents, and the influence of the organic solvents upon the electronic absorption spectra was studied. By applying the linear solvation energy relationship concept (*LSE*R), the effect of the solvent polarity and the formation of hydrogen bonds were interpreted. An estimation of the influence of the triazole derivatives structure upon their reactivity was done by determining the change of the characteristic absorption maximum depending on organic solvent, and a correlation was established with the *Hammett's* constants for the appropriate substitutions. An attempt was made to establish the correlation between the previously calculated acid-basic constants with the *Hammett's* constants for the appropriate substituents and to determine the degree and the influence of the resonant and inductive effects of the substituents.

Using the QSAR methods, an attempt was made to establish the correlation between the results obtained for the biological activity of the selected compounds, with the calculated values of the constants of protonation, as well as with appropriate physical-chemical (electronic, steric and hydrophobic) parameters.

**Key words:** 1,2,4-triazoles; protonation; dissociation; protic and aprotic solvents; *LSE*R; *Hammett's* constants; QSAR method.

(27. II 2006)

**Svetlana Aleksandar Risteska**

#### THE INFLUENCE OF COMPOSITION AND TEMPERATURE ON DEFORMATION FEATURE OF ALMG-ALLOYS

**Abstract:** The share of Al-alloys increases continuously, and materials with better mechanic, chemical and technological characteristics than that of pure aluminium are being sought.

A) The results of the research on deformation performance of AlMg<sub>5</sub>, AlMg<sub>3</sub> and AlMgSi<sub>0.5</sub> alloys, at temperature range of 22–200 °C and compression rate-upsetting rate of 5,50 and 100 mm/min, are presented here. The investigations of the mechanical features were performed under the conditions of single-axes pressing, type SCHENCK-Hydrauls PSB. The investigation of the material structure was performed by optic metallographic and TEM.

During the deformation discontinuities have been noticed and their appearance and disappearance depends on the temperature range and the upsetting rate.

Dynamic deformation aging is a process of reinforcement of metals, emerging as an effect between dissolved atoms and dislocations, recognized as Portevin-Le Chatelier's effect. Dynamic

deformation aging emerges during deformation by tension, pressure and torsion at defined temperature range and deformation rate. After reaching certain deformation level, so-called critical point of upsetting, the discontinuities appear and are noticed by x-y coordinate writer as picks on force-reduction curve ( $F-\Delta h$ ), of the machine itself.

This work presents the basic features determining the discontinuities  $E_c$ ,  $E_k$ ,  $\Delta\sigma$  and  $\Delta\epsilon$ .

The influence of different parameters on discontinuous relaxation of polycrystal materials illustrates certain consistency which is not the case with the monocrystals. With previous theoretical studies it is difficult to explain certain phenomena like experimentally obtained activating energy that very often does not correspond to the value of activating energy of gaps' diffusion in the basic metal. For the time being this deviation is explained by the assumption that the diffusion conducts movement in pairs, not of separate gaps, or it is considered as the energetic link between the gaps and dissolved atoms.

It should be pointed out that Cottrell's theory has considerable success in explaining the emergence of discontinuous relaxation in many inter and substituting alloys, but in spite all it was not able to explain many details of discontinuous relaxation, even when steel was in question. Probably it is connected with many undisclosed processes for transport of dissolved atoms and the method of their separations on dislocation points, or possibly because of the lack of the corresponding model.

B) This work also presents the results of experimental determination of resource of plasticity and tension state during the forge of all three alloys.

The experimental model for determination of metal plasticity with free forge pressing of cylindrical samples of AlMg<sub>5</sub>, AlMg<sub>3</sub> and AlMgSi<sub>0.5</sub> was researched. As plasticity criteria the model of Messis-Hencky-tension intensity of abstraction was used, and Kolmogorov's theory of fragility of metals during the upsetting. The experiments were performed as deformation of cylindrical test tube at different reduction levels up to 70% by the hydraulic pressing machine. During the deformation, the upsetting level was directly determined by reduction of height and force required to reach the defined upsetting level, but implicating the upsetting reinforcement, while the change in shape size, parameters of the resistance on deformation on state of tension after the upsetting. The tension parameters were determined on the bases of Messis-Hencky theory.

**Key words:** AlMg alloys; reinforcement curve; serrated yielding; deformation discontinuities; sensitivity to of deformation; activating energy; free forging; resources; temperature; upsetting rate reduction

(30. V 2006)

## Aleksandra Porjazoska-Kujundžiski

### DEGRADABLE MULTICOMPONENT SYSTEMS, BASED ON POLY( $\alpha$ -HYDROXY ACIDS), POLY( $\alpha$ -AMINO ACIDS) AND SOME BIFUNCTIONAL POLYESTERS AND POLYETHERS

(Synthesis, characterization and possible application as controlled drug delivery systems or matrices for tissue engineering)

**A b s t r a c t:** Several biodegradable and biocompatible multicomponent polymer systems, suitable for cell growth matrices, or systems for sustained, controlled and targeted drug delivery, have been synthesized.

1. A series of poly(DL-(L-)lactide-*co*-glycolide) (PDLLGA, PLLGA) with different molar masses has been synthesized by a ring-opening polymerization, using stannous octoate as catalyst. The corresponding copolymers were characterized with gel permeable chromatography (GPC), proton magnetic resonance ( $^1\text{H}$  NMR), Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC).

Porous and nonporous films were prepared from these copolymers, and their hydrolytic degradation was studied in phosphate buffer (PBS) (pH 7,4, at 37 °C), through mass and molar mass loss. Also, an attempt was made to estimate the possibilities to study the thermal aging (at 37 °C in vacuum oven) of poly (DL-(L-)lactide-*co*-glycolide) (PDLLGA; PLLGA) films by means Impedance Spectroscopy (IS) and Dielectric Thermal Analyses (DETA).

Poly(lactide-*co*-glycolide) copolymers were mainly, synthesized to be used further on as a part of block copolymer structures or corresponding blends, as well as one of the referent (comparable) substrates for cell growth. However, as these copolymers are of primary significance for biomedical application of their own, therefore an attempt was made to use them to fabricate microparticles as systems for controlled drug delivery.

Preparation of microparticles with or without encapsulated bovine serum albumin (BSA) was performed with copolymers with different molar masses, using double emulsion water-in-oil-in-water (w/o/w) method. The influence of the copolymers' molar mass, composition and molar lactide/glycolide ratio in the copolymers on the microparticles' size, morphology, yield, degradation rate, loading efficiency and release profile were studied.

It was also attempted to obtain BSA-loaded microparticles using solid-in-oil-in-water (s/o/w)

preparation method, and to demonstrate the influence of the preparation technique on the protein activity preservation.

2. Polymers mechanical properties, and especially their elasticity become an important issue when used for preparation of tissue engineering matrices with different structures, for maintenance of the structural integrity, and for promotion of the vascularization of the developing tissue. In order to improve the elasticity of poly(lactide-*co*-glycolide) copolymers, their blends with polycaprolactone-poly(dimethyl siloxane)-polycaprolactone (PCL-PDMS-PCL) (TEGOMER) triblock copolymer were prepared. The characterization of blends was performed by FTIR, DSC, mechanical stress-strain analyses, scanning electron microscopy (SEM), and their hydrolytic degradation was performed in phosphate buffer (pH 7,4, at 37 °C). The blends were used as matrices for proliferation of L929 mouse fibroblasts. The influence of TEGOMER on morphological characteristics and degradation rate of blends was shown, as well as that of the matrices to the cell affinity and growth.

3. Poly(L-lactide)/polyglycolide/poly(dimethyl siloxane) (PLLGA/TEGOMER) terpolymers have been synthesized by the ring-opening polymerization of L-lactide and glycolide with  $\alpha,\omega$ -amine-terminated poly(dimethyl siloxane) as prepolymer and macroinitiator, using stannous octoate as a catalyst. Terpolymers were characterized with GPC,  $^1\text{H}$  NMR, FTIR and DSC. Porous films were produced using a solvent-casting, particulate leaching technique. *In vitro* degradation of porous films was studied in phosphate buffer (PBS) (pH 7,4, 37 °C), followed by intrinsic viscosity, changes in mass, molar mass, and ratio lactide/glycolide/TEGOMER (determined by  $^1\text{H}$  NMR). Cell growth experiments using Swiss 3T3 fibroblasts showed that the copolymerization of PLLGA with TEGOMER influences the interactions of cells with polymer surface, with reference to the improvement of the biocompatibility of polymer systems.

4. Block copolymers with different hydrophobic/hydrophilic balance have been prepared. Namely, ABA triblock copolymers, where A = poly(lactide-*co*-glycolide), and B = poly(ethylene glycol) have been synthesized by the ring opening polymerization of lactide and glycolide using poly(ethylene glycol) as a macroinitiator and stannous octoate as a catalyst. The copolymers were characterized with GPC,  $^1\text{H}$  NMR, FTIR, DSC and thermogravimetric analyses (TGA). On the basis of the cell growth experiment (L929 fibroblasts) it is supposed that the quantity of PEG in these copolymers is too high, preventing in this way the adhesion and proliferation of cells. The blending with PCL was undertaken to decrease the hydrophilicity of the system.

5. Blends composed of poly(DL-lactide)-poly(ethylene glycol)-poly(DL-lactide) (PDLLA-PEG-PDLLA) and poly( $\epsilon$ -caprolactone) (PCL) were characterized with FTIR, DSC, TGA and contact angle measurements. *In vitro* hydrolytic degradation of copolymers and blends was performed in PBS (pH 7.4, at 37 °C), through the changes in intrinsic viscosity, mass and molar mass, indicating that blends with the biggest percentage of PCL have the smallest degradation rate. The cell growth experiments, have shown that these blends are suitable as matrices for attachment and growth of L929 fibroblasts, where the number of cells on the blends' surfaces is bigger than that of the copolymer' surface.

6. An introduction of functional groups, for example amino groups, into the polymer chain was expected to increase the affinity towards bioactive molecules, such as proteins and peptides. Thus, a terpolymer of poly(L-lactide)/poly(ethylene glycol)/poly(L-aspartic acid), (PLLA/PEO/PAsp) was synthesized by ring opening polymerization of  $\beta$ -benzyl L-aspartate N-carboxyanhydride, Asp(OBzl)-NCA with  $\alpha,\omega$ -hydroxy terminated triblock PLLA/PEO/PLLA copolymer as a macroinitiator. The resulting terpolymer was characterized with: FTIR, DSC,  $^1\text{H}$  NMR, TGA and "environmental" SEM. In order to improve the mechanical and physical properties, the rigid and brittle PLLA/PEO/PAsp terpolymer was blended with high molecular weight poly(L-lactic-co-glycolic acid) copolymer, PLLGA (85/15) ( $M_n = 45\,500$  g/mol,  $M_w = 95\,000$  g/mol). The hydrolytic degradation experiments were performed in PBS, pH 7.4, at 37°C. *In vitro* cell growth experiments confirmed that (PLLA/PEO/PAsp)/PLLGA blends are suitable as matrices for the attachment and proliferation of a significant amount of cells, but their number was slightly higher than that on the PLGA copolymer's surfaces. Consequently, there emerged the idea to modify PLGA copolymer with protein, for example collagen. It was expected that the bigger number of amino groups would improve the interactions between cells and polymer matrix (Number 7).

7. A carboxyl-ended triblock copolymer PEG-PDLLGA-PEG was synthesized in two steps: first, reacting poly(ethylene glycol)-*bis*-(carboxymethyl) ether with thionyl chloride to obtain an acyl chloride terminated poly(ethylene glycol) and subsequently coupling this compound to hydroxyl terminated poly(DL-lactide-co-glycolide), PDLLGA. The newly ended carboxyl groups of PEG-PDLLGA-PEG were further reacted with N-hydroxysuccinimide (NHS) in the presence of the bifunctional cross-linking agent, dicyclohexylcarbodiimide (DCC). PEG-PDLLGA-PEG and its active form, NHS-PEG-PDLLGA-NHS were characterized with GPC, FTIR, and  $^1\text{H}$ -NMR. The coupling of collagen type I to NHS-PEG-PDLLGA-NHS was performed in phosphate buffer, and corresponding product was analyzed using FTIR. Cell growth of L929 mouse fi-

broblasts, using PDLLGA, NHS-PEG-PDLLGA-PEG-NHS and PEG-PDLLGA-PEG, modified with collagen, as matrices, has shown that introduction of collagen significantly can increase the number of cells on the copolymer' surface.

8. Biodegradable and water insoluble copolymers composed of long hydrophobic polylactide blocks and short hydrophilic polyether blocks are suitable for the preparation of tissue engineering matrices and hard particles for controlled delivery of active substances. On the other hand, multiblock copolymers containing short polyester and long polyether blocks show self-assembling properties in aqueous solution; they form micelles with a structure suitable for prolonged and controlled drug release. Therefore, our further experiments were focused on the synthesis of water soluble block copolymers with short polylactide blocks, having amphiphilic properties. Pentablock poly(DL-lactide)-*b*-poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide)-*b*-poly(DL-lactide) copolymers, with different polylactide length, were synthesized by the ring-opening polymerization of DL-lactide initiated by poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymer (Pluronic<sup>®</sup>), as a macroinitiator, using one of the following catalysts: CsOH-H<sub>2</sub>O, CaH<sub>2</sub>, Ca(NH<sub>3</sub>)<sub>6</sub> and Sn(Oct)<sub>2</sub>. The resulting copolymers were analyzed with GPC,  $^1\text{H}$  NMR, FTIR, and their aqueous solution properties were determined by cloud point (CP) and critical micelle concentration measurements, using dye solubilization method. Transmittance electron microscopy (TEM) was used for particle visualization.

9. The idea of functionalized copolymers based on poly(lactide) was expanded to the synthesis of polyglycidol-*b*-poly(ethylene oxide)-*b*-poly(DL-lactide) (PG-PEO-PDLLA) triblock copolymers, containing a big number of hydroxyl groups. These copolymers form stable functionalized micelles in aqueous solutions. The hydroxyl groups of polyglycidol blocks located at the micelle surface provide high functionality, which could be used in further chemical modification resulting in a potential drug targeting agents. Triblock copolymers were characterized with GPC,  $^1\text{H}$  NMR, and the micellization process of the copolymers in aqueous media was studied by hydrophobic dye solubilization, static and dynamic light scattering, and transmission electron microscopy.

**Key words:** biodegradable and biocompatible (co)polymers and blends; poly(DL-(L)-lactide-co-glycolide); polycaprolactone-poly(dimethyl siloxane)-polycaprolactone;  $\alpha,\omega$ -amine-terminated poly(dimethyl siloxane); poly( $\epsilon$ -caprolactone); poly(ethylene glycol)/poly(ethylene oxide); poly(L-aspartic acid); Pluronic<sup>®</sup>; polyglycidol; matrices for tissue engineering; microspheres; micelles; functionalized micelles.

(12. VII 2006)

Blagoj Rizov

THEORETICAL AND PRACTICAL ASPECTS  
OF LIQUID ALUMINUM-SOME TRANSITION  
METALS INTERACTION

**A b s t r a c t:** In this thesis, interaction between liquid aluminum and some transition metals (Ni, Cr, Mn), was investigated from three main aspects: dissolution of the solid metals in liquid aluminum, mechanisms of intermetallics formation, and sequence of appearance at the interface. Due to the frequent use of nickel as alloying element in aluminum alloys, the great interest for nickel aluminides and the typical behavior of their formation, the main attention has been paid to the Al-Ni system. Thermal effects generated by exothermic solid nickel- liquid aluminum interaction were studied.

Laboratory and semi-industrial investigations have been performed in the temperature range between 750–1150 °C and the interaction time of up to 1200 seconds in normal and reductive atmosphere. For investigation in reductive atmosphere, special experimental procedure was applied using a tube shaped graphite device, designed especially for the purpose of this work. Coreless induction furnaces were used for melting, preheating and holding. Laboratory experimental conditions were set up to correlate with semi-industrial operational procedures for production of master alloys with high percentage of transition metals (5–20 wt. %). Intermetallics formed at the solid-liquid interface were studied by scanning electron microscopy, microprobe analysis and X-ray diffraction.

The results show that dissolution of transition metals (Ni, Cr, Mn) takes place in the presence of intermetallics on the solid-liquid interface. The intermetallics formation and the sequence of formation depend on temperature, time of interaction and concentration of transition metal in the melt. For a specific temperature, the first intermetallic to form is one which is in equilibrium with the melt, according to the equilibrium phase diagram for the corresponding system. The thickness of the intermetallics increases with time and concentration of the transition metal in the melt.

On the basis of the results from our study, and the experimental evidence and thoughts in the number of publications, a new adopted model based on effective concentration approach has been proposed for prediction of intermetallics formation during solid transition metal-liquid aluminum interaction.

The results of laboratory and semi-industrial investigations present useful data for defining the most important parameters for optimal technological procedure in the production of Al-Ni master alloys.

**Key words:** transition metals; liquid aluminum; intermetallics; solid-liquid metal interaction; dissolution; thermal effects; master alloys.

(18. X 2006)

Zagorka I. Koneska

ELECTROCHEMICAL PROPERTIES  
OF ZIRCONIUM IN H<sub>3</sub>PO<sub>4</sub> AND NaOH  
SOLUTIONS

**A b s t r a c t:** Subject of interest in this thesis was formation of Zr oxide films at different conditions and characterization of the formed oxides. Zr oxides were formed at open circuit potentials (OCP) as well as at anodic polarization in H<sub>3</sub>PO<sub>4</sub> and NaOH solutions (0,05–10 mol·dm<sup>-3</sup>) at room temperatures. Zirconium surfaces were subjected to mechanical or chemical polishing or cathodic polarization. Standard electrochemical techniques were used for electrochemical investigations.

Research was focused on three main topics:

(i) Behavior of Zr at open circuit potentials. Regularities of OCP dependence on the type and concentration of used electrolyte were studied in details.

(ii) Optical characteristics, i.e. optical constants  $n$  and  $k$  of both Zr substrate and oxides were determined by means of ellipsometry. The same technique was applied for determination of the thickness of oxide films formed spontaneously in H<sub>3</sub>PO<sub>4</sub> and NaOH (in-situ and ex-situ conditions), as well as ZrO<sub>2</sub> formed by anodization in the potential range of 0 – 65 V. The thicknesses of in-situ spontaneously formed films were 1.36 nm in 1 M H<sub>3</sub>PO<sub>4</sub>, 1.23 nm in 1M NaOH and 3.5 nm in 0.1M NaOH, while in ex-situ conditions the corresponding thicknesses were 4.88, 4.1 and 4.84 nm, respectively. Two potential ranges of different film growth rate were distinguished. Up to 12 V compact anodic films were formed; while above this potential porous ones appeared. In the former potential range NaOH formed films are thicker than the H<sub>3</sub>PO<sub>4</sub> in both conditions, but the electric field is stronger in H<sub>3</sub>PO<sub>4</sub> formed films.

(iii) The structure of anodically formed ZrO<sub>2</sub> films was studied by means of metallography and Raman spectroscopy. In both media, H<sub>3</sub>PO<sub>4</sub> and NaOH, amorphous oxides formed. Crystalline oxide (monoclinic phase) was determined in NaOH formed when a spark was produced during the anodization, thus crossing spot temperature increase due to the passing of high current.

According to the determined film characteristics, the Point Defect Model (PDM) provides better oxide growth description than the classical High Field Model (HFM) does.

**Key words:** zirconium; oxides; anodic oxidation; electrochemistry; ellipsometry; Raman spectroscopy

(25. X 2006)

IRENA MICKOVA

ELECTROCHEMICAL OPTICAL AND  
STRUCTURAL PROPERTIES OF ANODICALLY  
FORMED NIOBIUM OXIDES

**A b s t r a c t:** By cyclic voltammetry, polarization measurements, photocurrent measurements ellipsometry and Raman spectroscopy, the electrochemical, semiconducting, optical and structural properties of niobium and its passive and anodic oxide films formed in solutions of H<sub>2</sub>SO<sub>4</sub> were investigated.

Cyclic voltammetry was used for studying the redox reactions that occur during the cyclic change of potential. The formed passive films are stable in all investigated concentrations of H<sub>2</sub>SO<sub>4</sub> from 0.1 to 10 M, while in KOH at concentration of 2 M to 10 M, the reactivation process appears and destruction of passive films occurs.

It was shown that the passive and anodic films formed on niobium surfaces are the semiconductors of *n*-type in which the band gap energy and flat bend potential decrease with film thickness. Comparative investigations were also carried

out on thermally formed films and in the same film the *p* and *n*-type semiconductor appears as a result of various mechanisms of oxidation.

The optical constants and thickness of anodic oxide films formed in 1 M H<sub>2</sub>SO<sub>4</sub> and 1 M KOH were determined by ellipsometric measurements. The mathematical model for determining the film thickness and optical constants was utilized. It was calculated that the film grows faster in 1 M KOH and had a little bit higher complex refractive index than in 1 M H<sub>2</sub>SO<sub>4</sub>.

The kinetic analysis of the film thickness growth of anodic oxide films with times showed logarithmic law confirming the relatively high homogeneity of the even at anodic voltage at 80 V.

The structure of passive and anodic oxide films in the voltage region from 0 to 150 V in 1 M H<sub>2</sub>SO<sub>4</sub> and from 0 to 92 V in 1 M KOH was investigated by Raman spectroscopy. It was shown that the passive films were amorphous and the process of crystallization was initialized at voltage of 10 V.

**Key words:** niobium; niobium oxides; passive films; cyclic voltammetry; photocurrent measurements; ellipsometry; Raman spectroscopy

(14. XII 2006)

МАГИСТЕРСКИ ТРУДОВИ ОДБРАНЕТИ  
НА ТЕХНОЛОШКО-МЕТАЛУРШКИОТ ФАКУЛТЕТ ПРИ УНИВЕРЗИТЕТОТ „СВ. КИРИЛ И МЕТОДИЈ“  
ВО СКОПЈЕ, 2006 ГОДИНА

**Василевиќ Анета**, Реолошко однесување на асфалтен битумен модифициран со полимер/полимерна смеса (*Rheological behaviour of asphalt bitumen modified with polymer/polymer based blends*), 3. II 2006.

**Аџиски Ранко**, Контролирана порозна структура на стакло-керамика од металуршки троски (*Controlled porous structure of glass-ceramics from metallurgical slags*), 2. III 2006.

**Маринковски Мирко**, Извлекување на тешки метали од отпадни води со адсорпција на активен јаглен и природен зеолит (*Heavy*

*metals removal from waste water with adsorption on actived carbon and natural zeolite*), 12. IV 2006.

**Стаматовска Викторија**, Синтеза и испитување на ефектите на растворувачите на ултравиолетовите спектри на *N*-арил супституирани лаурамиди (додекамиди) (*Synthesis and investigations of solvent effects on the ultraviolet absorption spectra of N-aryl substituted lauramides (dodecanamides)*), 19. V 2006.

**Nofitovska Маја**, Методологија на проектирање квалитет на конфекциски производи (*Methodology for quality design of the apperal products*), 29. IX 2006.

СПЕЦИЈАЛИСТИЧКА РАБОТА  
ОДБРАНЕТА НА ТЕХНОЛОШКО-МЕТАЛУРШКИОТ ФАКУЛТЕТ  
ПРИ УНИВЕРЗИТЕТОТ „СВ. КИРИЛ И МЕТОДИЈ“ ВО СКОПЈЕ,  
2006 ГОДИНА

**Темелковски Владо**, Проектирање на стандардни оперативни процедури во претпријатие за производство на адитиви за градежништво (*Design of standard operational procedures in the enterprises for production of building aditives*), 11. IX 2006.

## ДИПЛОМИРАНИ СТУДЕНТИ НА ТЕХНОЛОШКО-МЕТАЛУРШКИОТ ФАКУЛТЕТ ПРИ УНИВЕРЗИТЕТОТ „СВ. КИРИЛ И МЕТОДИЈ“ ВО СКОПЈЕ, 2006 ГОДИНА

### Базно неорганско инженерство

2087.	Савов Милан Перо	6 февруари
2096.	Димчевска Стојан Соња	28 февруари
2114.	Бошевска Марко Јасмина	18 април
2116.	Кижески Наташа Александар	20 април
2119.	Стоилковска Димитрија Бисерка	27 април
2124.	Ковачевски Лазо Горан	12 мај
2131.	Јакшиќ Милан Ружица	12 мај
2138.	Змејков Змејко Иван	16 јуни
2139.	Ѓурчиновски Божин Даме	21 јуни
2188.	Стојменовски Василчо Дејан	30 октомври
2198.	Ѓоргиев Кири Тони	21 декември
2203.	Максимов Теохар Методи	27 декември

### Керамичко инженерство

2174.	Стојчева Благој Елизабета	29 септември
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### Базно органско и полимерно инженерство

2081.	Муртиши Садик Мартинеш	11 јануари
2089.	Милосављевски Миливоје Томица	7 февруари
2098.	Стојановска Љупчо Гордана	30 јануари
2099.	Јанчевска Борис Билјана	9 март
2100.	Стојановска Стојан Лидија	16 март
2111.	Шегмановиќ Стојан Даниел	14 април
2125.	Димковска Тодор Маја	19 април
2132.	Стефановска Ангелко Даница	13 јуни
2134.	Велковска Драги Марија	20 јуни
2136.	Тасковска Благоја Фросина	29 септември
2140.	Пенев Пене Валериј	23 јуни
2152.	Ашкапова Јанко Марија	7 јули
2153.	Велеска Миле Билјана	6 јули
2172.	Трајковска Димче Доња	25 септември
2177.	Тојтова Трпе Катерина	5 октомври
2187.	Јовановска Методи Билјана	14 ноември
2195.	Дуранска Бранко Даниела	7 декември
2199.	Смилески Стојан Дејанчо	22 декември
2202.	Дукоска Борис Елизабета	19 декември

### Прехранбено и биотехнолошко инженерство

2092.	Хаџи-Крстева Трајко Јасмина	16 февруари
2108.	Стефановска Вањо Ана	6 април
2117.	Петреска Благоја Аница	26 април
2118.	Јаневска Славко Жаклина	27 април
2122.	Пешевски Момчило Горан	27 април
2127.	Мицевски Атанас Венцо	5 јуни
2128.	Ламбеска Тина Соња	7 јуни
2129.	Анастасијевиќ Тина Маја	7 јуни
2137.	Митевска Стоилко Даниела	22 јуни
2143.	Ѓорчевска Борис Фросина	29 јуни
2145.	Хаџи Паунова Методије Љупка	29 јуни
2156.	Илиќ Трајче Александар	7 јули
2160.	Радњанска Дамјан Марија	7 јули
2181.	Неделкова Стојан Љубинка	20 октомври
2182.	Кракутовска Јован Татјанка	26 октомври
2189.	Стаматовска Цветко Снежана	20 ноември
2201.	Митиќ Влајко Наташа	25 декември

### Прехранбена технологија

2123.	Лазаров Ристо Петар	4 мај
2146.	Донев Страхил Ристо	30 јуни
2148.	Славков Душко Марјан	3 јули
2149.	Јовеска Благој Ана Марија	30 јуни
2150.	Илијоска Светозар Ивана	30 јуни
2158.	Мукаетова Зоран Ирена	7 јули
2159.	Христов Симеон Христо	10 јули
2161.	Јовановски Јован Михајло	10 јули
2171.	Мицевска Стојмир Благоица	26 септември
2184.	Костурска Бранко Ирена	6 ноември
2205.	Таневска Александар Славица	25 декември

### Биотехнологија

2141.	Илијева Љупчо Благоица	27 јуни
2163.	Јанкова Благој Билјана	11 јули
2164.	Сапламаева Панде Слаѓана	11 јули

### Петрохемиско инженерство

2088.	Петрески Гаџе Марјан	20 јануари
2097.	Тасева Кирил Валентина	6 март
2101.	Ивановски Благоја Круме	17 февруари
2103.	Стојановска Томислав Биљана	23 март
2110.	Трајановска Ванче Снежана	13 април
2121.	Симоновски Љупчо Наум	3 мај
2126.	Конески Илија Драган	29 мај
2133.	Комдовски Марко Коста	13 јуни
2147.	Дукадиновска Крсто Мирјана	3 јули
2196.	Талевски Мендо Сашо	6 декември
2204.	Недева Ристо Христина	28 декември
2208.	Чичоски Станко Горан	27 декември

### Дизајн и менаџмент во хемиската индустрија

2151.	Златевска Николче Илинка	6 јули
2157.	Старковска Наумче Јаглика	3 јули
2167.	Величковиќ Стојанче Александар	10 јули
2168.	Сараќинчева Јани Нешка	7 септември
2192.	Јаневска Звонко Јасмина	22 ноември
2194.	Збиљиќ Милорад Сретен	23 ноември

### Текстилно инженерство

2082.	Анастадова Ѓорѓи Јулијана	11 јануари
2091.	Атанасова Димитар Викторија	12 февруари
2104.	Тешовиќ Богдан Моника	30 март
2109.	Бошнакова Аџо Надица	13 април
2142.	Трајановски Блаже Тони	27 јуни
2162.	Барјактаров Јашар Орхан	10 јули
2170.	Емрула Сеид Ѓулшен	21 септември
2183.	Петрова Бојан Весна	7 ноември
2206.	Пановска Раде Јасминка	27 декември

### Конфекциско инженерство

2090.	Трајанова Иван Костадинка	17 февруари
2093.	Арнаутова Зоран Љубица	17 февруари



2107. Стојанов Анчо Тодор	30 март	<b>Екстрактивно металуршко инженерство</b>	
2112. Арсова Фиданчо Анета	17 април	2102. Пановска Благој Јасминка	22 февруари
2113. Тасески Никола Горан	18 април	2135. Трпков Петар Оливер	21 јуни
2115. Јанев Лазо Стојанче	20 април	2180. Сарагинов Благој Зоран	12 октомври
2120. Арсовска Кирчо Славица	28 април	<b>Екстрактивна металургија</b>	
2130. Петрова Васил Ана	9 јуни	2154. Стојановскио Мите Зоран	7 јули
2144. Јованова Дамјан Марина	29 јуни	2200. Михаилов Јован Стојче	26 декември
2155. Радуловска Димче Десанка	7 јули	<b>Преработувачко металуршко инженерство</b>	
2165. Јанчевска Младен Маја	14 јули	2086. Арсоска Михајло Наталија	3 февруари
2169. Попова Павле Соња	18 септември	2094. Мохамед Махмоуд Абабнех	28 февруари
2173. Тушевска Благој Марјана	25 септември	<b>14 Преработувачка металургија</b>	
2175. Трајаноска Слободан Благица	3 октомври	2166. Филиповиќ Драгиша Миодраг	14 јули
2176. Калајџиева Гордан Тијана	27 септември	2197. Димовски Лазар Ѓоре	19 декември
2178. Кондев Љупчо Борјан	25 октомври		
2185. Цветкова Панте Сузана	9 ноември		
2186. Сараќинчева Јани Маја	10 ноември		
2190. Воинова Александар Даниела	14 декември		
2191. Антоловиќ Андрија Марија	22 ноември		
2193. Стевчевска Ѓорѓи Маја	21 ноември		

**DOCTORAL THESIS  
DEFENDED AT THE STS CYRIL AND METHODIUS UNIVERSITY, THE INSTITUTE OF CHEMISTRY,  
FACULTY OF NATURAL SCIENCES AND MATHEMATICS IN SKOPJE, 2006**

**Biljana Pejova**

**CHEMICAL DEPOSITION, OPTICAL  
AND PHOTOELECTRICAL PROPERTIES  
OF THIN FILMS OF SEMICONDUCTING  
NANOCRYSTALLINE MATERIALS**

**A b s t r a c t:** In this PhD thesis, chemical methods for deposition of several nanocrystalline semiconductors in thin film form were developed. The structural, optical, electrical and photoelectrical properties of the synthesized materials were investigated. The systems studied included four binary semiconducting compounds: ZnSe, SnSe, Bi<sub>2</sub>S<sub>3</sub>, In<sub>2</sub>S<sub>3</sub>, as well as two ternary semiconductors: AgBiS<sub>2</sub> and CuInS<sub>2</sub>. Besides the chemical methods, also sonochemical routes to Bi<sub>2</sub>S<sub>3</sub>, In<sub>2</sub>S<sub>3</sub>, AgBiS<sub>2</sub> and CuInS<sub>2</sub> were also utilized, irradiating the reaction systems by a high-intensity ultrasonic probe (100 W/cm<sup>2</sup>) with frequency of 20 kHz using a direct-immersion ultrasonic horn. The average crystal size values of the studied systems deposited in thin film form and as bulk precipitate from the same reaction system, determined on the basis of intrinsic broadening of the diffraction maxima (using the approach of Debye-Scherrer), confirmed their nanocrystalline character and the predominance of the cluster mechanism of crystal growth. Heterogeneous sonochemical effects were found to lead to average crystal size decrease in all of the studied systems, while the post-deposition annealing led to average crystal size increase. Multiple regression analysis techniques were used to

perform a refinement of the unit cell parameter values of the synthesized materials and to derive conclusions about the existence of lattice strain. On the basis of the measured spectral dependencies of the absorption coefficient of the studied materials in thin film form, conclusions about the corresponding band structures were derived and the band gap energies were calculated on the basis of Fermi's golden rule for band-to-band transitions, employing parabolic approximation for the dispersion relation. The evolution of these quantities upon thermal annealing of the films was studied as well. Due to the nanocrystalline character of the studied films and the spatial confinement of charge carriers' motion within semiconductor quantum dots, the band gap energies of as-deposited materials were found to be blue-shifted with respect to the macrocrystalline values. Red shifts of the absorption onsets were observed upon annealing, accompanied by irreversible disappearance of size quantization effects. The sub band gap absorption of the studied films was investigated as well. In the case of ZnSe and CdSe, temperature dependencies of the band gap and Urbach energies were studied and interpreted employing concepts of contemporary solid state physics. Temperature dependencies of electrical resistivity of the films were measured and these data were used to calculate the thermal band gap energies as well as the impurity levels ionization energies. Changes in thin films' resistivities upon average crystal size increase were used to estimate the changes of barrier heights at intercrystalline boundaries. In the case of films manifesting internal photoelectric effect,

the spectral dependencies of stationary photoconductivity were measured. On the basis of these data, further conclusions about the band structures of the studied semiconductors were derived, employing several approaches. Photoconductivity relaxation dynamics in the studied systems, upon interaction with short light impulses, was also investigated. By analysis of the oscilloscopically measured relaxation curves, conclusions were derived about the charge carriers' recombination mechanisms and the average lifetimes of the photocarriers (*i.e.* relaxation times) were calculated. Lux-ampere characteristics of the photoconductors were measured and analyzed as well. On the basis of these investigations, conclusions about the potential applicability of the studied materials were derived.

**Key words:** semiconductors; thin films; quantum dots; chemical deposition; sonochemical deposition; band structures; optical properties; electrical properties; impurity level ionization energy; photoconductivity; Urbach energy; photoconductivity relaxation dynamics.

(18. I 2006)

**Janko Temelkov**

#### CHEMICAL COMPOUNDS OF BILE CALCULI AND OTHER CHARACTERISTICS OF BILLIARY CALCULOSIS IN THE POPULATION OF REPUBLIC OF MACEDONIA

**A b s t r a c t:** Surgical removal of lithogenic bile in patients in Republic of Macedonia is rising by 8–12 % each year for the past 20 years and is considered to be the most frequent abdominal operation. In order to determine the main characteristics of cholelithiasis in R. M. we performed chemical analysis of bile excretions and gallstones in 201 samples obtained after surgical removal in our group of patients. The patients in our group of interest live in different territories of the state that were defined as 6 regions with different specifics: Skopje and Kumanovo, Tetovo, Gostivar and Debar, Prilep, Bitola and Kavadarci, Veles, Štip and Gevgelija, Strumica and Valandovo. The age of patients was between 20 and 70 years. The greatest number of women in our group of patients, 66,3 % were in the ages between 41 and 55. The greatest number of men in our group of patients, 71,4 % were in the ages between 46 and 60.

Cholelithiasis was 4,7 times more frequent in women than in men.

The most frequent factors that influence the appearance and rise of the disease in our examined group of patients is: stress with 83 %, overeating and obesity 60,6 %, familial influences and genetic predisposition 32,8 %, nutritional reasons: eating a lot of food rich in fat and also, greater number of pregnancies.

According to the results of the examinations of the lithogenic bile in the group of 190 samples, 90 % had lower mass parts of water. In 55,5 % in the sediment of the bile we found crystals of cholesterol and grains of Ca-bilirubinate. In 59 % the ration of micellary state was in disorder, which provided existence of two and more physical phases in the system.

The most frequent constituent of the gall stones is cholesterol with values of 38,5 – 99 W/% mass parts, then bilirubin with 0,05 – 41,2 W/%. The chemical analysis of the bile calculi in the patients with cholelithiasis showed pure cholesterol type in 6,95 %, cholesterol type in 66,2 %, mixed type of calculi, made of cholesterol and bilirubin in 22,38 % and bilirubin type of calculi in 4,47 % of the patients. Calculi with greater mass part of bilirubin were found in the group of patients from the southern parts of the country: Prilep, Bitola and Kavadarci, Veles, Štip and Gevgelija, Strumica and Valandovo.

Hematological results showed that most of the parameters were within the reference values. In 67 % of the patients the blood levels of cholesterol were above the higher reference value. The values of triglycerides in the blood were above the higher reference value in 41 % of the patients. Higher values for the enzymatic activity for AST, ALT, AP and  $\gamma$ -GT were observed in 16 % of the examined group of patients.

**Key words:** cholelithiasis; chemical; compounds; gallstones; cholesterol; bilirubin; bile excretions; bile sediment; risk factors

(26. IV 2006)

**Goran Stojković**

#### INVESTIGATION OF THE REACTIONS OF PROTONATION OF SOME AMIDES IN HIGHLY ACIDIC MEDIA WITH UV SPECTROSCOPY

**A b s t r a c t:** In this work, the protonation of ten aliphatic amides of the type  $R-C(O)-NR'_2$  (when  $R=H, Me$ ;  $R'=H, Me, Et, i-Pr, i-Bu$  and  $Bu$ ), and eleven aromatic amides (methyl-, chloro-, nitrosubstituted benzamides in *meta* and *para* position, benzanilide and three benzotoluidides) in sulphuric acid media was studied by UV spectroscopy in the 190–350 nm region. Characteristic vector analysis was successfully applied to separate the effect of protonation from the medium effect for aromatic, unlike aliphatic amides where CVA failed because of the hypsochromic shift of the protonated base under 190 nm. The first characteristic vector (CV) captures about 95–98 % of the variance and the second CV ~100 % of the cumulative percentage variance in the region 200–350 for benzamides and 210–350 nm for benzanilides.

The dissociation constants and the solvation parameters  $m^*$  and  $\phi$  were calculated using the excess acidity method and Bunnett-Olsen method. The  $pK_{BH}^+$  values of aromatic amides obtained with  $H_A$  function are in satisfactory agreement with those calculated with previously mentioned methods. For acetamides which are stronger bases and should be protonated at lower acidity, EAM obtained worse results.

When the Hammett's equation was applied on the investigated formamides and acetamides, in any possible combination of Taft's constants, no satisfactory correlation was gained. From the Taft's approach, it can be concluded that the polar effect is insignificant compared to the steric effect. The  $pK_{BH}^+$  values of benzamides were correlated with structure using the Hammett ( $\rho = -0.91$ ) and Taft approach. It was found that for both substituted benzamides (*meta* and *para*) the inductive effect is more relevant than the resonance one. The basicity of the benzanilides is increasing following this substituents order:  $H < m\text{-Me} \approx p\text{-Me} < o\text{-Me}$ .

Furthermore, it was presented that Counter-Propagation Artificial Neural Networks optimised by employment of genetic algorithms could be satisfactory used for  $pK_{BH}^+$  values prediction for the investigated group of compounds.

**Key words:** UV spectroscopy; formamides; acetamides; benzamides; benzotoluidides; protonation constants; Hammett-Taft correlations;  $pK_{BH}^+$  prediction.

(7. VI 2006)

**Petre Makreski**

#### STUDY ON THE VIBRATIONAL SPECTRA OF SOME OXIDE, SULFATE AND SILICATE MINERALS

**A b s t r a c t:** Vibrational spectra of seven oxide, six sulphate and sixteen silicate minerals (seven nesosilicates and nine inosilicates) originating from the Republic of Macedonia were studied. The infrared spectral investigations were carried out for the following oxide minerals: hematite, magnetite, limonite, goethite, corundum, rutile and chromite. In addition to the absorption in the far infrared region it was sometimes necessary to record the mid IR spectrum (for example, limonite, goethite). A pronounced frequency difference for the bands originating from the same mode was found in the IR spectrum of the mineral with high refraction index (e.g. rutile). The studied powder X-ray diffraction patterns of the minerals were used to provide a rapid check of the purity of the mineral, as well as to identify the present impurities. Strong correlation between the content of the determined elements in the mineral and the mineralogical characteristics of

its locality was found. Identification of the sulfate minerals: anhydrite, brochantite, chalcantite, potassium alum and epsomite using vibrational (infrared and Raman) spectroscopy was unambiguous. Due to the present quartz impurity being detected by both vibrational techniques, difficulties were encountered in the characterization process of jarosite. It was found that the infrared spectra could distinguish between the studied hydroxide and hydrate sulfate mineral. Namely, the  $\nu(\text{OH})$  spectral region of the OH-containing minerals brochantite,  $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$ , and jarosite,  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ , is characterized by the appearance of narrow and better separated bands as compared with the  $\nu(\text{H}_2\text{O})$  spectral region of the studied hydrated minerals: potassium alum,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , chalcantite,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and epsomite,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  where complex broad band appears. In fact, these bands served as an evidence of the strength of the hydrogen bonding. Namely, it was found that the shift of the centroids of the  $\nu(\text{H}_2\text{O})$  bands to lower frequencies corresponds to the increase of the hydrogen bonding strength in the structures of the studied minerals. On the other hand, more pronounced discriminating features for the studied OH-containing sulfate minerals were provided by the study of the spectral region of their internal  $\text{SO}_4$  modes. The identification of the studied nesosilicates: almandine, spessartine, zircon, titanite and kyanite by vibrational (IR and Raman) spectroscopy was unequivocal, whereas some difficulties appeared in the identification process of staurolite and olivine (forsterite or fayalite) specimens. It was shown that, even when higher-wavelength excitation line (1064 nm rather than 514 nm) was used, the laser power could cause substantial Raman spectral changes, as was the case with the studied almandine sample. Although an inversion centre is present in the space groups of the studied pyroxene (augite, carpholite and ferrojohansennite), pyroxenoid (bustamite and rhodonite) and amphibole minerals (glaucophane, arfvedsonite, tremolite-actinolite and hornblende), IR-Raman doublets were observed. Their appearance was explained by the presence of so called, tetrahedral-octahedral-tetrahedral (TOT) strips in the structures whose stacking sequence symmetry dominates over the crystal symmetry and determines the activity of the normal modes. It was also found that higher wavenumbers of the characteristic  $\nu(\text{XO}_6)$  modes in the IR spectra of the pyroxenes compared to the lower wavenumbers of the corresponding mode in the spectra of pyroxenoids could be used to discriminate between pyroxenes and pyroxenoids. Furthermore, it was found that the number of the IR bands in the  $800\text{--}650\text{ cm}^{-1}$  region is the same with the number of the tetrahedra in their repeating unit. In the case of amphiboles, the number of IR bands in the  $\nu(\text{OH})$  region was used to determine the number of the different

cation types in the mineral because it was found that the presence of different Y cations in various octahedral sites causes differences in the spectral picture. However, variation of the extent of the sensitivity to impurities between the two vibrational

techniques justifies their simultaneous application, confirming their complementary.

**Key words:** infrared, Raman, vibrational, spectra, powder X-ray diffraction, oxide, sulfate, silicate minerals.

(11. VII 2006)

**МАГИСТЕРСКИ ТРУДОВИ  
ОДБРАНЕТИ НА ИНСТИТУТОТ ЗА ХЕМИЈА НА ПРИРОДНО-МАТЕМАТИЧКИОТ ФАКУЛТЕТ  
ПРИ УНИВЕРЗИТЕТОТ „СВ. КИРИЛ И МЕТОДИЈ“  
ВО СКОПЈЕ, 2006 ГОДИНА**

**Виолета Иванова**, Разработка на методи за определување на резидуални мономери ослободени од забарски пломби и лекови во биолошки флуиди со високоефикасна течна хроматографија (*Development of methods for determination of residual monomers released from dental materials and drugs in biological fluids using high-performance liquid chromatography*) 5. V 2006.

**Сани Демири**, Избор и дизајн на хемиски експерименти во оптичка проекција за наставата по хемија за прва и втора година гимназиско образование (*Selection and design of overhead projector chemical experiments for the first and second grade high-school education*) 10. V 2006.

**Милена Јанкуловска**, Определување на константите на дисоцијација на некои незаситени карбоксилни киселини во силно кисела средина (*Determination of dissociation constants of some unsaturated carboxylic acids in strong acid media*) 8. VI 2006.

**Сандра Димитровска Лазова**, Структурни корелации кај различни изоморфни серии од типот на перовскит (*Structural correlations at various isomorphous series of the perovskite type*) 9. VI 2006.

**Сања Костадиновиќ**, Квалитативна и квантитативна анализа на есенцијални масла од кората на портокал, лимон и мандарина со употреба на гасна хроматографија (*Qualitative and quantitative analysis of essential oils of the peel of orange, lemon and mandarin using gas chromatography*) 13. VII 2006.

**Јожица-Мајда Бундалеска**, Концентрирање и определување на вкупната содржина и на хемиските форми на елементи во траги во води со атомска апсорпциона спектрометрија (*Concentration and determination of total content and chemical forms of trace elements in waters by atomic absorption spectrometry*) 10. X 2006.

**Мирјана Јанкуловска**, Однесување на нови деривати на 1,2,4-триазолин-3-тион во различни медиуми (*Behaviour of new derivatives of 1,2,4-triazoline-3-thione in different media*) 10. X 2006.

**Иван Серафимовски**, Определување на хемиските форми на арсен и жива во риба со примена на атомска апсорпциона спектрометрија (*Speciation analysis of different arsenic and mercury species by atomic absorption spectrometry*) 29. XII 2006.

**СПЕЦИЈАЛИСТИЧКИ РАБОТИ  
ОДБРАНЕТИ НА ИНСТИТУТОТ ЗА ХЕМИЈА НА ПРИРОДНО-МАТЕМАТИЧКИОТ ФАКУЛТЕТ  
ВО СКОПЈЕ ВО 2006 ГОДИНА**

**Вангелица Енимитева**, Примена на кобалт(III) тетраметилендитиокарбамат како колектор за кофлотационо концентрирање на елементи во траги и нивно определување со атомска апсорпциона спектрометрија (30. VI 2006).

**Милена Тасеска**, Сепарирање на елементи во траги од минерали на бакар и железо и

нивно определување со атомска апсорпциона спектрометрија (3. VII 2006).

**Наташа Бакреска Кормушоска**, Застапеност на тешки метали во слатки води пред и по нивното пречистување (11. VII 2006).

**ДИПЛОМИРАНИ СТУДЕНТИ  
НА ИНСТИТУТОТ ЗА ХЕМИЈА НА ПРИРОДНО-МАТЕМАТИЧКИОТ ФАКУЛТЕТ  
ПРИ УНИВЕРЗИТЕТОТ „СВ. КИРИЛ И МЕТОДИЈ“  
ВО СКОПЈЕ, 2006 година**

<b>Наставна насока (дипломирани професори по хемија)</b>					
7457	Стојанческа Петре Силвана	1 февруари	5114	Тодоровска Драге Марина	18 октомври
2220	Јанкова Живко Жаклина	1 февруари	7491	Чавдаров Владимир Јордан	18 октомври
7463	Петрова Георге Марија	17 февруари	8659	Спирова Вите Марија	20 октомври
6843	Талевска Ѓоргија Оливера	1 март	8645	Николоска Никола Ирена	24 октомври
7459	Најдоска Љубомир Менче	20 април	8311	Настова Крсте Ирена	26 октомври
7675	Кочоска Никола Наташа	15 мај	4427	Василијадовска Павле Марија	30 октомври
6837	Јанкуловска Тоде Татјана	17 мај	6325	Спасовска Ѓорге Снежана	30 октомври
10682	Атанасовска Петре Александра	22 мај	8320	Кочкова Васил Катерина	31 октомври
10205	Николовска Дивание Сашка	29 мај	7134	Љатифи Јумни Аффрим	31 октомври
7452	Тасевска Борис Магдалена	16 јуни	5547	Радуловиќ Ѓоце Јасмина	31 октомври
6836	Сулејмани Дестан Флорије	19 јуни	7423	Филипова Илија Сашка	31 октомври
6500	Јакимовска Живко Елена	12 јули	8051	Милчева Драги Павлинка	3 ноември
5733	Антонијевска Слободан Љубинка	17 јули	8323	Трајкоска Илија Христина	29 ноември
6648	Ивановска Благоја Александра	1 септември	8310	Павлова Васил Марија	30 ноември
9282	Кленческа Адем Емина	4 октомври	8083	Николова Славчо Думеника	7 декември
8043	Кимевска Томислав Анита	10 октомври	9291	Петреска Стеван Јасмина	13 декември
7687	Стамениќ Драго Душица	27 декември	8063	Диманова Томе Васе	25 декември
			8663	Рашковска Славчо Александра	27 декември
			4698	Стојановска Кирил Биљана	28 декември

**Препаративна и аналитичко-структурна насока  
(дипломирани инженери по хемија)**

8652	Петрушевски Ѓоце Ѓорѓи	19 јануари
10200	Стојанческа Петре Силвана	1 февруари
8069	Димоски Ѓоце Јован	17 февруари
7708	Петкоска Петар Лидија	27 февруари
7126	Ахмети Хабиб Љаура	8 март
7697	Ристова Благојчо Снешка	17 март
6853	Малеска Крсте Добрила	31 март
7127	Николова Димче Петранка	5 април
7149	Цветаноска Киро Виолета	5 април
6331	Санева Душан Јасмина	11 април
6532	Донева Ѓорѓи Наташа	21 април
2785	Донева Драгољуб Драгица	8 мај
7480	Павлески Павле Никола	10 мај
6889	Спасовска Милорад Александра	11 мај
6525	Јовановски Томе Бојан	17 мај
6861	Ѓорѓиевска Љубе Зорица	18 мај
7705	Милевски Борко Игор	23 мај
7497	Анѓеловски Бранко Дејан	29 мај
7709	Стојкоска Јован Катерина	9 јуни
9288	Коцевски Стевчо Ванчо	28 јуни
10197	Кочоска Никола Наташа	3 јули
5771	Спиркоска Живко Билјана	3 јули
8321	Спиркоска Бранко Ели	10 јули
6539	Богојевски Борко Тодор	12 јули
1961	Алексова Бранко Емилија	14 јули
8664	Волканоски Косте Стојанче	14 јули
9084	Ивановска Живко Габриела	15 јули
5753	Јованческа Русе Анета	15 септември
5750	Кузмановска Веле Маја	20 септември
7124	Стојановски Спасо Александар	26 септември
7489	Илијоски Борис Диме	2 октомври
6868	Стојановска Трајан Емилија	2 октомври
8056	Божиновска Крсто Маја	16 октомври

**Насока  
аналитичка биохемија  
(дипломирани инженери по хемија)**

8681	Кракутовска Ѓорѓи Марија	16 јануари
8679	Тренчевска Стојан Олгица	16 јануари
8986	Саздова Љупчо Катерина	17 јануари
8677	Матеничарска Јован Зорка	15 февруари
8678	Бујароска Ѓорѓија Билјана	4 мај
9056	Петковска Миле Ана	12 мај
8684	Соколовска Тоде Фросина	17 мај
8990	Костовска Славе Верче	29 мај
8683	Милановска Миле Алесонора	31 мај
8673	Станојков Стојче Александар	6 јули
8665	Илоска Никола Дијана	30 октомври

**Наставна насока  
(дипломирани професори по биологија–хемија)**

7627	Исмаиловски Јонуз Идрис	24 јануари
8352	Селмани Исак Линдита	2 февруари
6592	Серафимоска Гаврил Татјана	3 февруари
8226	Анастасова Борис Ана	6 март
8339	Митева Блажо Драгица	5 април
9020	Трагачевска Раде Марија	25 мај
6982	Витанова Зоран Емица	7 јуни
8347	Таири Таир Лаура	7 јуни
8348	Кроси Џеват Ардита	9 јуни
8888	Мангоска Милчо Наташа	16 јуни
7613	Андрески Димитрија Владо	23 јуни
8894	Шавреска Науме Христина	26 јуни
8893	Ѓорѓиевска Љупчо Сунчица	25 септември
9030	Андреевска Симо Биљана	26 септември
9025	Андреевска Симо Блага	26 септември
7610	Бандулиев Димитар Милан	29 септември
7798	Ончевска Раде Драгана	3 октомври
8885	Лазароска Симон Билјана	5 октомври
8242	Сасанска Благој Марија	6 октомври
6074	Поп-Димитрова Ѓорѓе Марија	20 октомври

8884	Наумоска Кири Даниела	25 октомври	9448	Петровска Звонко Цветанка	31 октомври
7796	Јовановска Стојмир Мирјана	27 октомври	6469	Стојчевска Стојан Наталија	31 октомври
7801	Каили Нафо Беќим	30 октомври	7790	Тонева Љубе Слаѓана	31 октомври
7192	Азис Ибиш Назмије	30 октомври	7214	Фетаовска Скендер Ѓилтен	10 ноември
5021	Алексова Сандре Христина	31 октомври	6647	Каракашев Никола Андреј	12 декември

### ИЗВЕСТУВАЊЕ И ПОКАНА

Во периодот од 4 до 6 октомври 2007 во Институтот за хемија при Природно-математичкиот факултет во Скопје ќе се одржи

#### VII конгрес по чиста и применета хемија на студентите од Македонија (со меѓународно учество)

На Организациониот одбор му претставува задоволство да ги покани студентите од Македонија да земат активно учество на конгресот, со што ќе се отвори можност за размена на идеи, искуства и знаења помеѓу студентите и институциите.

Апстрактите ќе бидат прифаќани само во електронска форма, испратени на е-mail адресата: vlador@iupona.pmf.ukim.edu.mk. Авторите (и нивните ментори) преземаат целосна одговорност за содржината на апстрактите.

Учесниците се должни да платат котизација од 10 евра.

Со почит  
претседател на Организациониот одбор,  
асист. м-р Сандра Димитровска-Лазова

### КОНГРЕСИ И КОНФЕРЕНЦИИ

#### 2008 Winter Conference on Plasma Spectrochemistry

6 – 12 January 2008  
Temecular, CA, United States  
<http://icpinformation.org/>

#### PETROTECH 2008

14 – 16 January 2008  
Bahrain, Bahrain  
[www.confabb.com/conferences](http://www.confabb.com/conferences)

#### 40th Annual Canadian Mineral Processors Operators Conference

22 – 24 January 2008  
Ottawa, Ontario, Canada  
[www.min-eng.com](http://www.min-eng.com)

#### ExTech(R) 2008 — Tenth International Symposium on Advances in Extraction Techniques

28 – 30 January 2008  
Brugge, Belgium  
<http://www.ordibo.be/htc/index.html>

#### PITTCON 2008 — The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy

2 – 7 March 2008  
New Orleans, United States  
<http://www.pittcon.org/>

#### GEO 2008

3 – 5 March 2008  
Manama, Bahrain  
[www.geobahrain.org](http://www.geobahrain.org)

#### Chem05 — International Conference in Chemistry, Green and Sustainable Chemistry for Developing Countries

3 – 6 March, 2008  
Cairo, Egypt  
<http://chem05.cu.edu.eg/>

#### Heterocyclic Chemistry

9 – 12 March 2008  
Florida, USA  
[www.arkat-usa.org](http://www.arkat-usa.org)

#### Silicone Elastomers 2008

12 – 13 March 2008  
Munich, Germany  
[www.rapra.net](http://www.rapra.net)

#### 4th International Conference on Trace Element Speciation in Biomedical, Nutritional and Environmental Sciences

25 – 29 May 2008  
Neuherberg, Germany  
<http://www.gsf.de/spec/neu/index.php>

#### European Conference on Continuous Casting 2008

4 – 6 June, 2008  
Riccione, Italy  
[www.aimnet.it](http://www.aimnet.it)

#### 24th Annual Meeting of the Polymer Processing Society

15 – 19 June 2008  
Salerno, Italy  
[www.pps-24.com](http://www.pps-24.com)

#### 35th International Symposium on Environmental Analytical Chemistry ISEAC 35

22 – 26 June 2008  
Gdansk, Poland  
[http://www.iaeac.ch/iseac\\_symposium/iseac\\_home.html](http://www.iaeac.ch/iseac_symposium/iseac_home.html)

#### 2nd INTERNATIONAL CONGRESS ON CERAMICS

29 June – 3 July 2008  
Verona, Italy  
[www.ecers.org](http://www.ecers.org)

#### CHISA 2008

24 – 28 August 2008  
Prague, Czech Republic  
[www.chisa.cz/2008/](http://www.chisa.cz/2008/)

#### ESBES-7 — 7th European Symposium on Biochemical Engineering Science

7 – 10 September, 2008  
Ljubljana, Slovenia  
[http://events.dechema.de/ESBES\\_7.html](http://events.dechema.de/ESBES_7.html)

#### 2nd International IUPAC Conference on Green Chemistry

14 – 20 September 2008  
Moscow, Russia  
<http://venus.unive.it/inca/>

#### MS&T'08 — Materials Science and Technology 2008 Conference and Exhibition

21 – 25 September 2008  
Baltimore, Maryland, United States  
<http://www.matscitech.org/2007/home.html>

## САЕМИ И ИЗЛОЖБИ

**Heimtextil Frankfurt**

9 – 12 January, 2008

Frankfurt, Germany

<http://www.cosmoworlds.com/heimtextil.htm>**Sensors, Measurement and Instrumentation**

13 – 14 February, 2008

Birmingham, UK

[www.mteceexhibition.co.uk](http://www.mteceexhibition.co.uk)**The Minerals, Metals & Materials Society (TMS) Annual Meeting**

9 – 13 March, 2008

New Orleans, Louisiana, United States

[www.tms.org](http://www.tms.org)**Industrie Paris 2008**

31 March – 4 April, 2008

Paris, France, Metropolitan

<http://www.industrie-expo.com>**Tube 2008**

31 March – 4 April, 2008

Düsseldorf, Germany

<http://www.mdna.com/shows/tube.html>**The London Book Fair 2008**

14 – 16 April 2008

London, UK

[www.londonbookfair.co.uk](http://www.londonbookfair.co.uk)**Aluminium 2008 World Trade Fair & Conference**

23 – 25 September, 2008

Essen, Germany

<http://www.aluminium-messe.com>

## INSTRUCTIONS TO AUTHORS

The *Macedonian Journal of Chemistry and Chemical Engineering* (*Maced. J. Chem. Chem. Eng.*) is an official publication of the Society of Chemists and Technologists of Macedonia. It is published twice a year. The journal publishes **original scientific papers, short communications, reviews, professional and educational papers** from all fields of chemistry, chemical engineering, food technology, biotechnology and material sciences, metallurgy and related fields. The papers published in this *Journal* are summarized in *Chemical Abstracts*.

This journal also publishes, continuously or occasionally, the bibliographies of the members of the Society, book reviews, reports on meetings, information on future meetings, important events and dates, and various headings which contribute to the development of the corresponding scientific field.

**Original scientific papers** report unpublished results of completed original scientific research. Experimental data should be presented in a way that enables reproduction and verification of analyses and deductions on which the conclusions are based. Manuscripts should normally not exceed 6000 words.

**Short communications** should also contain completed but briefly presented results of original scientific research. Manuscripts should normally not exceed 2000 words.

**Reviews** are submitted at the invitation of the Editorial Board. They should be critical surveys of an area in which preferably the author himself is active. The reviews can be longer than typical research articles but should generally be limited to 10000 words including references, tables and figures.

**Professional papers** report on useful practical results that are not original but help the results

of the original scientific research to be adopted into scientific and production use. Manuscripts should normally not exceed 4000 words.

**Educational papers** report on the activities in the laboratory and classroom and the needs of the community of educators in all mentioned fields. Manuscripts should normally not exceed 4000 words.

## SUBMISSION OF MANUSCRIPTS

The authors bear the sole responsibility for the content of the contributions. It is assumed that by submitting their paper the authors have not violated any internal rules or regulations of their institutions related to the content of the contributions. Submission of a paper implies that it has not been published previously, that it is not under consideration for publication elsewhere, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, without the written consent of the Publisher.

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A cover letter must accompany every new submission. It should contain full names of all authors and their affiliation, the manuscript title and the name and contact information for the corresponding author. Please provide a mailing address, e-mail address, and phone and fax numbers. Authors are requested to submit, with the manuscript, the names and full contact details (including e-mail addresses) of 3 potential referees.

## PREPARATION OF MANUSCRIPTS

Prepare the entire manuscript in double-space typing, on numbered pages of A4 format with margins of 2.5 cm on each side. Do not use footnotes.

The papers should be written in the shortest possible way and without unnecessary repetition. The original scientific papers, short communications and reviews should be written in English. Professional papers may be also submitted in Macedonian. For the educational papers it is preferred to be written both in English and in Macedonian. Abstract and key words in Macedonian, respectively in English for the professional papers, must accompany each manuscript.

Manuscript should contain: title, authors names and addresses, abstract, key words, introduction, experimental or theoretical background, results and discussion, acknowledgement (if desired) and references.

**Title.** It should be brief and informative but should define the subject of the manuscript. It should include most of the key words.

**Authorship.** List the first and last name of each author. Omit professional and official titles. Give the complete mailing address of each author. For the corresponding author include an e-mail address and a phone and fax numbers. The name of the corresponding author should carry an asterisk.

**Abstract.** Each manuscript should be provided with an abstract of about 100–150 words. It should give the aim of the research, methods or procedures, significant results and conclusions. Define any abbreviations used in the abstract.

**Key words.** Up to 5 key words or phrases should be given to facilitate indexing and on-line searching.

**Introduction.** The most important previous results related to the problem in hand should be reviewed avoiding a detailed literature survey, and the aim and importance of the research should be clearly stated.

**Experimental section.** This section should contain a description of the materials used and methods employed in form which makes the results reproducible, but without detailed description of already known methods.

Manuscripts that are related to theoretical studies, instead of experimental section should contain a sub-heading **theoretical background** where the necessary details for verifying the results obtained should be stated.

**Results and discussion.** The authors should discuss their findings, postulate explanations for

the data, elucidate models and compare their results with those of other works. Irrelevant comparisons and speculations unsupported by the new information presented in the manuscript should be avoided. The conclusions should be not given separately but included in this section.

**Tables.** They should be given with a suitable caption and should be numbered consecutively with Arabic numerals. Footnotes to tables should be typed below the table and should be referred to by superscript lowercase letter. Each table should be typed on a separate sheet. The correct position of the tables should be marked on the manuscript.

**Figures.** Figures (photographs, diagrams and schemes) should be numbered consecutively with Arabic numerals in order to which they referred. They should accompany the manuscript but should not be imbedded in the text. Each figure should be clearly marked with the figure number and the first author's name. All figures should have captions that should be supplied on a separate sheet. Correct position of the figures should be marked on the manuscript. The size of the symbols for the physical quantities and units as well as the size of the numbers and letters used in the reduced figures should be comparable with the size of the letters in the main text of the paper. Each figure or group of figures should be planned to fit, after appropriate reduction, into the area of either one or two columns of text. The maximum finished size of a one-column illustration is 8.0 cm and that of a two-column illustration is 17.0 cm width. Make sure you use uniform lettering and sizing of your original artwork. All figures should be printed on a high quality graphics plotter. Figures should be also sent in electronic form as TIFF or JPG files with minimum 300 dpi or higher resolution.

Color illustrations in print can be included only at the author's expense.

**Units.** The SI (Systeme Internationale d'Unites) for quantities and units should be used throughout the whole text. If nomenclature is specialized, nomenclature section should be included at the end of the manuscript, giving definitions and dimensions for all terms.

The names of chemical substances should be in accordance with the IUPAC recommendations and rules or *Chemical Abstract* practice.

The results of elemental analyses of organic compounds should be given in the following form:

Anal. C<sub>12</sub>H<sub>16</sub>O (176.26).

Calc'd: C 81.77; H 9.15; O 9.08 %.

Found: C 81.63; H 9.36; O 9.01 %.



When a large number of compounds have been analyzed, the results should be given in tabular form.

**Formulas and equations.** Chemical equations should be balanced and numbered consecutively along with mathematical equations or other mathematical expressions. All of them should be marked with Arabic numerals in parenthesis in the right hand margin. The use of equation editor (Word) for typesetting the equations is recommended. Strokes (/) should not be used instead of parentheses.

**Acknowledgement.** Financial support, advice or other kinds of assistance can be included in this section.

**References.** Literature references should be numbered and listed in order of citation in the text. They should be selective rather than extensive with the exemption to review articles. Avoid references to works that have not been peer-reviewed. Citation of a reference as "in press" implies that it has been accepted for publication. Abbreviations of the titles of the periodicals should be in accordance with *Chemical Abstracts Service Source Index* (CASSI).

The surname of one or two authors may be given in the text, whereas in case of more than two authors they should be quoted as, for example, Julg *et al.* [1]. References should be cited as follows:

#### Journals:

- [1] P. Hobza, Z. Havlas, The fluoriform-ethyleneoxide dimer exhibits an antihydrogen bond, *Chem. Phys. Lett.*, **303**, 447–452 (1999).
- [2] I. Mladenoska, D. Nikolovska-Nedelkoska, E. Winkelhausen, S. Kuzmanova, *Aspergillus oryzae*  $\beta$ -galactosidase – an efficient catalyst for alkyl- $\beta$ -galactoside synthesis in organic mono-phased system, *Maced. J. Chem. Chem. Eng.*, **26** (1), 17–24 (2007).

#### Books:

- [1] J. A. Roels, *Energetics and Kinetics in Biotechnology*, Elsevier Biomedical Press, Amsterdam, New York, Oxford, 1983.
- [2] H. Chum, M. Baizer, *The Electrochemistry of Biomass and Derived Materials*, ACS Monograph 183, American Chemical Society, Washington, DC, 1985, pp. 134–157.
- [3] J. W. Finley, G. A. Leveille, Macronutrient substitutes, in: *Present Knowledge in Nutrition*, E. K. Ziegler, L. J. Filer Jr. (Eds), ILSI Press, Washington DC, 1996, pp. 581–595.
- [4] С. Хаџи Јорданов, *Корозија и заштитна на металиите*, Нова Македонија, Скопје, 1993.

#### Scientific meetings:

- [1] M. Gerales, L. Hcs, M. Araujo, A. Marcincin, The Application of new performance PP fibers in functional knit structure, *Proceedings of International Textile Clothing and Design Conference*, Dubrovnik, Croatia, 2002, pp. 59–64.

For the web references, as a minimum the full URL should be given. Any further information, if

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