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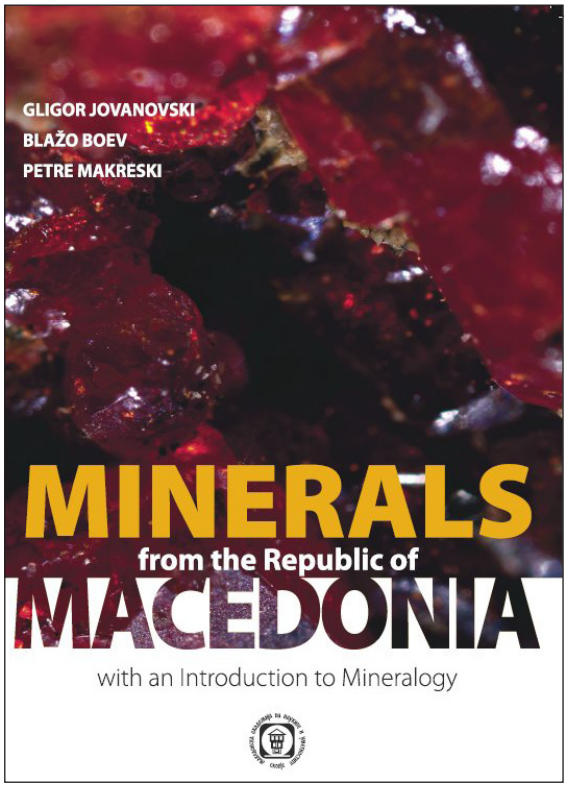
MINERALS FROM THE REPUBLIC OF MACEDONIA WITH AN INTRODUCTION TO MINERALOGY

by

Gligor Jovanovski, Blažo Boev and Petre Makreski
with continued contributions from Branko Kaitner, Trajče Stafilov and Bojan Šoptrajanov



The reviewed monograph is the first extended work in which data on the minerals of the Republic of Macedonia have been described. This book is written in English to make the information on the mineralogy of the Republic of Macedonia accessible to a worldwide audience. The monograph contains a general introduction to mineralogy, which makes it useful for people starting their education in this science, i.e. students of geology, amateur mineralogists and mineral collectors in the Republic of Macedonia. Thus, the monograph is a dual-purpose book.

The first part of the book is an introduction to mineralogy with the necessary connections to the related sciences of physics, chemistry and crystallography. The starting point is the keystone: what a mineral is, what mineralogy is and how minerals are formed. Furthermore, we see material on the crystallographic basis of mineralogy and a chapter devoted to the crystalline state of substances. The next point is on the chemistry of minerals. This significant chapter explains modern conceptions on the constitution of solids and the types of chemical bonds. An important part of the basis of mineralogy is the theory of isomorphism and solid solutions, which is also reflected in the monograph. The physical properties of minerals and an introduction to optical mineralogy are found in the next chapter. A long chapter is devoted to modern methods of mineralogical research, including physical assays such as X-ray diffraction and various spectroscopic methods as well as chemical analysis. The final chapter of the first part of the book presents the principles of the classification of minerals and some examples.

The second main part of the monograph contains collected information on the minerals of the Republic of Macedonia and their localities. A chapter is devoted to the general geological characteristics of the Republic of Macedonia. The four major geotectonic units of the territory, namely the West-Macedonian zone, the Pelagonian massif, the Vardar zone and the Serbo-Macedonian massif are described, focusing on mineragenetic aspects.

The next chapter seems especially valuable, as it includes a description of the most interesting mineral localities of the Republic of Macedonia (with a geographical map showing their distribution). This information was almost unknown to the worldwide community of both professional and amateur mineralogists and the monograph mainly fills in this blank. Among others, the descriptions of localities of global mineralogical significance are given. First, there is the famous Allchar, an unusual low-temperature hydrothermal Au-Sb-As deposit with incredibly rich and diverse thallium mineralization, a source of many new minerals and the location of a unique project on solar neutrinos. Alinci is a very

interesting location, as it is a group of alkali-syenite related occurrences: a new mineral, macedonite, or $PbTiO_3$, was first discovered here and several rare species have been found. Nežilovo, a belt of metamorphic and metasomatic rocks with unusual mineralogy and geochemistry, similar to the famous Långban in Sweden, is also described, focusing on the distribution of exotic complex oxygen compounds with Pb, Ba, Zn, Mn, Sb, Ti, As, *etc*., with endogene origin. Other outstanding objects characterized in the book are an ultrabasic complex with nickel deposits at Ržanovo, a polymetallic deposit related to manganese-rich skarns at Sasa, as well as the occurrence of nice, big crystals of pink corundum and even ruby in the marbles at Sivec. From the monograph, we can learn about remarkable finds of giant crystals at localities in the Republic of Macedonia such as epidote (up to 1 m), titanite, gypsum, *etc*.

The next chapter comprises of mineral descriptions where all mineral species and varieties known in the Republic of Macedonia are listed. The minerals are divided in two groups: the first, much larger group, is related to the studied and characterised minerals by the authors of the monograph, whereas the second group contains information concerning the non-collected minerals (in the monograph termed as *other minerals*). For each mineral, general data (chemical formula, symmetry, physical properties, occurrence, origin of the name, *etc.*) and information on its distribution in the Republic of Macedonia are given. Furthermore, for the studied minerals, quantitative chemical composition analysis, X-ray powder diffraction data with determined unit cell parameters, optical data and infrared and/or Raman spectrum are given. These characteristics were obtained from mineral samples collected in the Republic of Macedonia.

The last chapter includes a list of publications of the authors on the mineralogy of the Republic of Macedonia and indices of minerals and localities mentioned in the monograph. It is necessary to note that each chapter of the book contains a detailed list of references that is valuable in itself.

An important part of the monograph is the illustrations. Besides common figures necessary to describe basic concepts (especially in the first part, the introduction to mineralogy), we can enjoy many color photographs of minerals from the Republic of Macedonia, including nice full-page pictures. This seems valuable because the mineral specimens from this country are not well-known and not widespread in foreign museums and private collections, and readers will acquire considerable new information and impressions from these pictures. The high printing quality of the book merits praise.

Thus, I can recommend this monograph to a wide audience, from professional mineralogists and geologists to people who are taking their first steps in this field.

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DOCTORAL THESES

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1

Jožica Majda Serafimovska

DETERMINATION OF TOTAL CONTENT AND CHEMICAL SPECIES OF ANTIMONY, ARSENIC, SELENIUM AND TIN IN ENVIRONMENTAL SAMPLES WITH ATOMIC ABSORPTION SPECTROMETRY (5.3.2012)

The methods for determination of total contents and speciation of arsenic, antimony, selenium and tin in environmental samples using atomic absorption spectrometry were investigated.

The influences of EDTA, carboxylic acids, amino- and hydroxocarboxylic acids, monosaccharides and humic acids on the generation of arsines and stibines in HG-AAS were investigated. EDTA (0.02 mol/l), ascorbic acid (0.02 mol/l) and glucose or fructose (0.2 mol/l) are useful additives for leveling sensitivities for As(lll), monomethylarsonate (MMA) and dimethylarsinate (DMA). The presence of glycine, malonic, tartaric acids, BICIN and soil humin extracts leads to differences in analytical signal response between these As species. An analytical application to the determination of the sum of As(III), MMA and DMA as well as the sum of toxicologically relevant hydride forming As fraction As(lll) + As(V) + MMA + DMA in EDTA soil/sediment extracts using HG-AAS was demonstrated. The limit of detection was 0.2 mg/kg. EDTA, tartaric, citric and malonic acids, fructose and N,N-bis(2-hydroxyethyl)glycine (BICIN) were found as appropriate reaction media for selective and sensitive determination of Sb(III). The prereduction of Sb(V) to Sb(III) in the presence of organic ligands is quantitative with L-cysteine (1% *m/v*) as reductant. An analytical application to the determination of Sb(III) and Sb(V) in waters, tea infusions, EDTA soil and sediment extracts using continuous flow HG-AAS was demonstrated. The limit of detection was 0.08 μg/l. Within-day precision was 5–20% in the range 0.2–1 μg/l Sb and 4–12% in the range 1–5 μg/l Sb with recoveries between 94 and 102%.

A modified liquid phase semimicroextraction (LSME) was developed for preconcentration and determination of ultra trace levels of inorganic Sb species in waters using ETAAS. Sb(III) species were selectively extracted as dithiocarbamate complexes from 100 ml aqueous phase into 250 μl xylene at pH 5–8. Total Sb was determined by the same extraction with a pH of 0–1.2 without the prereduction of Sb(V) to Sb(III). The concentration of Sb(V) was obtained as the difference between that of total Sb and Sb(III). The enrichment factor of the method is 400 fold. The limit of detection was 2 ng/l Sb. Recoveries of spiked Sb(III) and Sb(V) in river, tap, and sea water samples ranged from 93 to 107%. The results for total Sb concentration in the river water reference material SLRS-5 were in good agreement with the information value. The method was applied for determination of dissolved inorganic species of Sb, Sn and Se in the river of Vardar and its main tributaries. The higher oxidation states of Sb and Se were found as the predominant form in the studied surface waters.

Fractionation analysis was performed to determine the distribution of Sb(III), Sb(V), Sb-bound to fulvic and Sb-bound to humic acids in soils. The applied procedures for fractionation included: extraction with 0.11 mol/l acetic acid (exchangeable fraction); extraction with 0.05 mol/l EDTA (exchangeable fraction); extraction with 0.1 mol/l NaOH (fulvic and humic fraction). Sb-bound to fulvic acid can be found into filtrate, while Sb-bound to humic acid is found into solid residue.

Keywords: arsenic, antimony, selenium, tin, water, soil, sediment, speciation analysis, EDTA fractionation, semimicroextraction, HG-AAS, ETAAS.

2

Maja Šišovska

DEVELOPMENT AND OPTIMIZATON OF HPLC METHODS FOR DETERMINATION OF PERMETHRIN AND ITS RESIDUES IN DIFFERENT MATRICES (14.3.2012)

The research presented in this work is contribution in the field of the new analytical methods for identification and quantification of permethrin [3-(2,2-dichloro-ethenyl)-2,2-dimethylcyclopropane-carboxylic acid-(3-phen-oxyphenyl) methylester] and its residues in various matrices. The proposed HPLC methods are for determination of its geometrical isomer forms (*cis* and *trans*) and its enantiomers (*R-cis*, *R-trans*, *S-cis* and *S-trans*). For the separations, chromatographic columns with various dimensions, stationary phases and particle size (LiChrosorb® RP18 (250 mm × 4 mm i.d., 5 μm), Chromolith® Performance RP18e (100 mm × 4.6 mm i.d., monolithic rod), Zorbax SB-C18 (50 mm × 4.6 mm i.d., 1.8 μm), Supelcosil Si 60 (150 mm x 4,6 mm i. d., 5 μm)) were used, and one column with chiral stationary phase on base of ß-cyclodextrin (ChiraDex® (250 mm × 4 mm, 5 μm)), among them. *n*-Hexane or mixtures of acetonitrile and water or methanol and water were used as mobile phases, in isocratic or gradient mode, with various volumetric ratio of the components, at various flow rates, by controlled temperature and detection at 215 nm or 220 nm.

The monolithic rod and 1.8 μm particle sized columns applicability was evaluated and their chromatographic parameters data were compared with data obtained for other column types. It was shown that for analysis, using monolithic column, less time is needed without loss in chromatographic performance and when using 1.8 μm particle size column the runtime is 4.5 min in normal and 1.6 min in rapid mode, using only 3.6 ml mobile phase.

All proposed methods are validated with regards to: retention and separation factors, resolution, linearity, limits of detection and quantification, accuracy and precision. The validation data show that the proposed methods are selective, sensitive, precise and accurate, and simple and rapid, as well.

When developing the method for permethrin residues analysis in wine, the quantity of the solvent (ethanol) needed for sample preparation has been optimized and the matrix effect studied, which is important when testing various types of wine.

As for the method for separation and quantification of permethrin enantiomers, the whole procedure is shorter and the separation of the *trans*-pair is achieved with better analytical performance compared to reported methods. The correlation between the temperature (288–318 K) and chromatographic parameters was studied. The obtained vant Hoff's correlations are presented (ln $k \times 1/T$) and (ln $\alpha \times 1/T$), for *cis* and *trans*-enatiomers and enantiomeric pairs. It was found that the first correlation is linear, and the second is linear in short range (318–303 K), only. At higher temperatures, *cis*-enantiomers are more stable compared to the *trans*-pair, but at lower temperatures the two enantiomeric pairs act similarly. The values for: ΔG^{o}, ΔH^{o} and ΔS^{o} were calculated for every enantiomer, separately. The obtained values of free Gibbs energy (ΔG^{o}) for the *cis*-pair are higher than the values obtained for the*trans*-pair, which results in better chiral separation. For the *trans*-pair, the ΔH^{o}-values are very similar, but for the *cis*-pair they differ more, leading to their better separation. Also, it has been calculated the free Gibbs energy difference ($\Delta(\Delta G)$) for the *cis* and *trans* pairs, for the temperature range 288–318 K. According to the results, both the entropy and the enthalpy have part in the separation, which is affected by many processes acting simultaneously in the separation of enantiomers. This method was applied for permethrin enantiomers testing in correlation with a temperature stability study in a tomato juice matrix.

Proposed methods have been applied for permethrin determination in various formulations (medical shampoo, veterinary powder, gel and powder for household use, mattresses cleaner) and raw material samples as well as for permethrin and residues determination in wine samples. It was proved that the same methods might be used for analysis of various formulations and matrices.

Keywords: permethrin, HPLC, *cis*-permethrin, *trans*-permethrin, monolithic HPLC column, permethrin formulations, residues, wine, tomato juice, permethrin enantiomers, chirality, b-cyclodextrin stationary phase, Van Hoff's correlations, entalphy, entrophy, Gibbs energy

3

Sani Demiri

CHEMICAL DEPOSITION AND CHARACTERIZATION OF INORGANIC ELECTROCHROMIC THIN FILMS (11.6.2012)

Five new chemical methods for deposition of electrochromic thin films of inorganic materials are designed. The developed methods are simple and do not require the use of special equipment and technique. The films are prepared on electroconductive FTO glass substrates and analyzed by different methods. The film composition and structure are determined by X-ray powder diffraction, infrared and Raman spectroscopy and differential thermal analysis. The surface morphology of the thin films is studied by SEM and AFM. The redox processes in different aqueous and non-aqueous electrolytes are examined by cyclic voltammetry. The electrochromic properties are characterized by VIS spectrometry. The prepared films comprise different chemical compositions: Prussian blue, sodium vanadium oxide bronzes, birnessite-type potassium manganese oxides, manganese(IV) oxides obtained by transformation of manganese(II) carbonate and hydrated tungsten(VI) oxide.

The Prussian blue thin films are easily prepared by successive immersion of the substrates into an acidic aqueous solution of $Fe_2(SO_4)_3$ and $K_4[Fe(CN)_6]$. These thin films exhibit stability, excellent reversibility and good electrochromic characteristics, which make these films favorable for electrochromic devices.

The electrochromic thin films of sodium vanadium bronzes have been prepared by mixing of aqueous solutions of sodium metavanadate and acetic acid. The thin films exhibit two-step electrochromism (color change from yellow-orange to green, and then to blue) related with the redox reactions between V^{5+} and V^{4+} ions acompanied with intercalation/deintercalation of alkaline ions from electrolyte.

The chemical deposition of potassium manganese oxide films has been performed at room temperature by a reaction of aqueous solutions of potassium permanganate and manganese(II) chloride. The manifested electrochromic behaviour of the films with color change between brown and pale-yellow is due to the electrochemical transformations between Mn^{4+} and Mn^{3+} ions. The aqueous KNO_3 is found to be the best electrolyte regarding the electrochromic characteristics of the thin films.

The manganese(II) carbonate thin films have been deposited precipitation using urea from aqueous solution of Mn^{2+} ions. The as-deposited $MnCO_3$ films are transformed into electrochromically active manganese(IV) oxide films by thermal treatment and electrochemical cycling.

The chemical bath deposition from solutions containing sodium tungstate and hydrochloric acid produces thin films of hydrated tungsten(VI) oxide. The electrochromic properties are significantly improved by use of sulfuric acid as electrolyte.

The achieved results for the studied inorganic thin films in respect to the difference in the transmittance between the bleached and colored states are promising for their application in different electrochromic devices.

Keywords: electrochromism, thin films; semiconductors; chemical synthesis; X-ray powder diffraction, SEM–EDS analysis, FTIR and Raman spectroscopy.

4

Jasmina Petreska Stanoeva

POLYPHENOLIC PROFILE AND ANTIOXIDANT ACTIVITY OF MOUNTAIN TEA OF GENUS *Sideritis* FROM THE BALKANS AND CHARACTERIZATION OF METABOLITES OF ITS POLYPHENOLS IN URINE

(6.7.2012)

Twenty one sample of Sideritis species (*S. scardica, S. raeseri, S. taurica, S. syriaca* and *S. perfoliata*) from various sites on the Balkan Peninsula were analyzed with regards to the nature and abundance of secondary metabolites, particularly phenolic compounds, which have several roles in the plant physiological processes and health beneficial effects. Also, the phenolic profile of different parts (leaf, flower and stem) of wild and cultivated grown Sideritis species from Macedonia has been analyzed using water and methanol extracts to give an insight in the nature and content of various polyphenols.

A systematic method for phenolic compounds identification, using tandem mass spectrometry coupled to high performance liquid chromatography with diode array detection was developed. The characterization of each phenolic compound was performed using MS/MS product-ion analysis and common–neutral-loss analysis. The structures of flavonoid glycosides were analyzed before and after alkaline hydrolysis and the effect of sugar substitution and acetylation on the flavonoids and ESI ionization and fragmentation discussed.

Three new phenylethanoid glycosides, alyssonoside, echinacoside, and forsythoside were detected for the first time. The occurrence of the hydroxycinnamic acids, phenyletahnoid glycosides and flavonoids has been investigated in taxonomically related taxa of the genus *Sideritis*. All taxa analyzed produced very similar phenolic patterns characterized by the presence of 5-caffeoylquinic acid, forsythoside B, verbascoside, hypolaetin 7-O-[6‴-O-acetyl]-allosyl(1→2) gluco¬side, apigenin, 7-(4”-p-coumaroylglucoside) and 4’-O-methylisoscutellarein 7-O-[6‴-O-acetyl]-allosyl(1→2)glucoside and minor amounts of isoverbascoside, apigenin 7-O-allosyl(1→2) glucoside, isoscutellarein 7-O-allosyl-(1→2)-[6″-O-acetyl]-glucoside hypolaetin 7-O-allosyl-(1→2)-[6″-O-acetyl]-glucoside and 4’-O-methylhypolaetin 7-O-[6‴-O-acetyl]-allosyl-(1→2)-[6″-O-acetyl]-glucoside. These results show that these species are systematically very closely related. Phenylethanoid glucosides and flavonoid acetylglucosides are dominant and they present 90 % of total phenolic compounds. Principal component analysis (PCA) was performed for the nature and content of the different compounds to be correlated to the particular species of the genus *Sideritis* and also to the locations. The antioxidant capacity was measured with three methods (DPPH·, $ABTS^{\cdot+}$ and FRAP assays) and was linearly correlated with phenolic content. Concerning the phenolic content in the different aerial parts, leaf was the richest plant organ in phenolics followed by flower and stem with the lowest amount.

A nutrition experiment was performed for studying the bioavailability of the polyphenols from Sideritis with healthy human subjects, who consumed *S. scardica* decoction after which urine was collected and analyzed. 63 metabolities were identified using HPLC/MSn, which were mainly glucuronide, sulphated and methylated metabolities. The identification and structure elucidation of these metabolities provided essential data for further pharmacological and clinical studies of Sideritis polyphenols bioavailability.

The application of an ion trap mass spectrometer, usually employed for identification, was systematically evaluated for quantitative analysis of various conjugated forms of flavonoids and compared to UV quantification using nine referent standards of flavonoids with six different aglycones. The analytical characteristics of the tested MS methods were shown to be comparable to UV with regards to precision and accuracy and superior for selectivity and sensitivity. Moreover, it was shown that in MS detection one flavone derivative can be quantified using other available

derivatives with similar substitution pattern with regards to sugars attached and acetylated sugars whereas the nature of the aglycone is not essential.

Keywords: Sideritis, mountain tea, flavonoids, phenolic compounds, PCA, antioxidant activity LC-MS/MS, ion trap, quantification

5

Sandra Atanasovska-Lazova

SYNTHESIS AND INVESTIGATION OF STRUCTURE AND PROPERTIES OF SOME COMPLEX PEROVSKITES (18.9.2012)

In this doctoral dissertation, the results of the synthesis and investigation of four perovskite series of general formula: $RCo_{1-x}Cr_xO_3$ (R = Y, Pr, Gd); $YCo_{1-x}Fe_xO_3$; $Pr_{1-x}A_xCo_{0.5}Cr_{0.5}O_3$ (A = Bi, Pb) and $Y_{0.8}Ca_{0.2}Co_{0.5}Fe_{0.5}O_3$, are presented. In general, the solution combustion method was used for synthesis of the perovskites, but with different fuels and, in some cases, with previous gel formation. The obtained perovskites were identified with X-ray powder diffraction and their crystal structures were refined using the Rietveld method. The morphology of the perovskites was analyzed by SEM, and their electrochemical and catalytic properties were investigated by cyclic voltammetry.

It was shown that the solution combustion is an appropriate method for synthesis of these series of perovskites, but for some of them the use of glycine as a fuel (for example, the Pr-series), was more successful, for some other it was urea (the Gd and Y series) and $YCo_{1-x}Fe_xO_3$ series was obtained via citrate precursor synthesis. The complex perovskites – those with two cations in B-position and those with substitution in A-position – are new synthesized, namely, no literature data for these compounds were found.

In order to find out the influence of the applied method of synthesis on the morphology and dimensions of the particles of the obtained perovskites, the SEM images were recorded. It could be concluded that the perovskites within these series are of the same morphology, consisted of nanoparticles joined in aggregates with porous structure. The additional heating of the particles leads to increasing of the dimension of the particles.

The X-ray diffraction patterns show that the obtained perovskites are orthorhombic, and crystallize within the space group Pnma. The crystal structure refinement (undertaken by the Rietveld method), as well as, the crystallochemical calculations, have shown that in these perovskites, there are two main reasons for deviation of the ideal perovskite structure. Namely, in all of the obtained perovskites octahedral tilting is evident, however in some of them (for example, the $PrCo_{1-x}Cr_xO_3$ series) in cases when the content of Co^{3+} exceeds that of Cr^{3+}, besides the octahedral tilting, a more pronounced distortion of the octahedron is evident due to the deformation of the B-O distances. This could be due probably to some changes in the spin state of Co^{3+} ion, and also to the influence of A-cation on octahedral distortion.

The electrochemical and the catalytic properties of the obtained perovskites were investigated by cyclic voltammetry. The results of the analysis of these properties in different electrolytes showed that these perovskites (except the $RCrO_3$ perovskites) exhibit pronounced catalytic activity toward chloride ions and towards basic solutions. In the first case, the perovskites catalysis the oxidation of the chloride ions and in the second case the catalytic oxidation of the hydroxide ions followed with evolution of oxygen. The electrochemical investigation of the systems of KOH and methanol showed that these materials exhibit catalytic influence to the oxidation of methanol in basic media.

Keywords: complex perovskites, solution combustion method, X-ray diffraction, Rietveld method, SEM, cyclic voltammetry

6

Mirjana Jankulovska

INVESTIGATION OF ACID-BASE EQUILIBRIA OF SOME NEWLY SYNTHESIZED ARYLHYDRAZONES OF SUBSTITUTED BENZHYDRAZIDES (19.9.2012)

Three series of p-substituted aromatic hydrazones have been synthesized by condensation of benzhydrazide/p-substituted benzhydrazides (–CH_3, –OCH_3, –Cl and –OH) with benzaldehyde/ *p*-substituted benzaldehyde (–OCH_3 and –NO_2). Initially, p-substituted esters were prepared from benzoic acid, p-substituted benzoic acid and methanol. In the second step, p-substituted hydrazides were prepared from the previously synthesized esters and hydrazine hydrate. Finally, p-substituted aromatic hydrazones were obtained from hydrazides and benzaldehyde or p-substituted benzaldehyde. The identification of the synthesized hydrazones was confirmed by the following techniques: ^{1}H NMR, ^{13}C NMR, IR and UV-Vis spectroscopy and element analysis (CHN). Using the concept of linear salvation energy relationship (LFER) based on mono and the dual substituent parameters, quantitative assessment of the substituent effects on the substituent chemical shifts was made.

The spectral behavior of some *p*-substituted aromatic hydrazones was examined by the UV-Vis spectroscopic technique in the pH region and the acid-base equilibriums was characterized qualitatively and quantitatively. The UV-Vis spectra of the solution at different pH were studied and the position of the absorption maximum was defined in neutral, acidic and basic media, and the electron transitions were discussed, too. It was confirmed that the protonation and dissociation processes take place in one step. The exceptions are hydrazones which contain phenolic group in theirs molecules. The changes in the UV-Vis spectra were utilized for determination of the concentration dissociation constants graphically and numerically. The pKBH+ and pKHA/pKH2A values were determined from the absorbance values of experimental and reconstructed spectra obtained by characteristic vector analysis (CVA). In order to obtain thermodynamic pKBH+ values measurements were performed at ionic strengths of 0.1 mol/dm^3, 0.25 mol/dm^3 and 0.5 mol/dm^3. Furthermore, the influence of the substituents on the changes of the UV spectra, as well as, on the values of the dissociation constants was discussed.

The site of protonation in the hydrazone molecule was determined using the values of proton affinity, while the site of the dissociation of the proton could be predicted using deprotonation enthalpy values. These parameters were found with the quantum-chemical calculations using AM1 and PM3 semiempirical methods. Also, the stability of the unprotonated and protonated isomers (E and Z) which exist in the solution was discussed.

Keywords: *p*-substituted aromatic hydrazones, synthesis, influence of substituents, NMR, IR, UV-Vis spectrophotometry, protonation, dissociation, concentration dissociation constants, thermodynamic dissociation constants, semiempirical methods (AM1 and PM3)

MASTER THESES

DEFENDED AT THE INSTITUTE OF CHEMISTRY, FACULTY OF NATURAL SCIENCES AND MATHEMATICS, Ss. CYRIL AND METHODIUS UNIVERSITY IN SKOPJE, 2012

МАГИСТЕРСКИ ТРУДОВИ

ОДБРАНЕТИ НА ИНСТИТУТОТ ЗА ХЕМИЈА НА ПРИРОДНО-МАТЕМАТИЧКИОТ ФАКУЛТЕТ ПРИ УНИВЕРЗИТЕТОТ СВ. КИРИЛ И МЕТОДИЈ ВО СКОПЈЕ ВО 2012 ГОДИНА

1. **Рашковска Славчо Александра,** Карактеризација на византиска и отоманска глазирана керамика со спектроскопски и дифракциски техники.
   Raškovska Slavčo Aleksandra, Characterization of Byzantine and ottoman glaze ceramics using spectroscopic and diffraction techniques. (2.3.2012)

2. **Сефер Зумбер Бирхан,** Електрохемиска студија на пренос на електрони и јони низ течно-течна меѓуфазна гранична површина со примена на површински модифицирани електроди.
   Sefer Zumber Birhan, Electrochemical study of electron and ion transfer across liquid-liquid interphase by means surface modified electrodes. (2.3.2012)

3. **Тодоровиќ Војислав Дејан,** Развој на метода за идентификување на компонентите од издувните гасови на мотори со внатрешно согорување.
   Todorović Vojislav Dejan, Development of method for identification of the components in exhaust fumes of engines with internal combustion. (7.3.2012)

4. **Бујароска Ѓорѓија Билјана,** Теоретски студии на хидратација на аминокиселини во водни раствори со секвенцијален Монте-Карло квантномеханички пристап.
   Bujaroska Gjorgjija Biljana, Theoretical studies of hydration of amino acids in aqueous solutions using the sequential Monte-Carlo quantum mechanical approach. (6.4.2012)

5. **Ставревска Стевчо Наташа,** Експерименти во ново руво.
   Stavrevska Stevčo Nataša, Experiments in a novel dress. (29.5.2012)

6. **Станкоска Миле Катерина,** Електрохемија на сахарин на течна меѓуфазна гранична површина – модел за проучување на пренос на сахарин низ клеточни мембрани.
   Stankoska Mile Katerina, Electrochemistry of saccharin at the liquid-liqiud interface. A model for the transfer processes of saccharin across cellular membranes. (4.9.2012)

7. **Јанчовска Ѓорѓи Маја,** Анодна стрипинг волтаметрија на цинк, кадмиум и олово на бизмут филм електроди.
   Jančovska Gjorgji Maja, Anodic stripping voltammetry of zinc, cadmium and lead at bismuth-film electrodes. (12.11.2012)

8. **Лазаревска Благоја Елена,** Разработка на методологија за определување на фенолниот профил на аронија од Македонија со употреба на спектрофотометрија и течна хроматографија со масена спектрометрија.
   Lazarevska Blagoja Elena, Development of methodology for determination of the phenolic profile of aronia from Macedonia using spectrophotometry and liquid chromatography coupled to mass spectrometry. (13.11.2012)

9. **Наумова Мијалче Галаба,** Развој на едноставен волтаметриски метод за мерење на антиоксидативниот капацитет на растителни масла.
   Naumova Mijalče Galaba, Development of a simple voltammetric method for determination of the antioxidant capacity of vegetable oils. (14.11.2012)

SPECIALISATION WORKS

COMPLETED AT THE INSTITUTE OF CHEMISTRY, FACULTY OF NATURAL SCIENCES AND MATHEMATICS, Ss. CYRIL AND METHODIUS UNIVERSITY IN SKOPJE, 2012

СПЕЦИЈАЛИСТИЧКИ ТРУДОВИ

ОДБРАНЕТИ НА ИНСТИТУТОТ ЗА ХЕМИЈА НА ПРИРОДНО-МАТЕМАТИЧКИОТ ФАКУЛТЕТ ПРИ УНИВЕРЗИТЕТОТ СВ. КИРИЛ И МЕТОДИЈ ВО СКОПЈЕ ВО 2012 ГОДИНА

1. **Митрески Наумче Илија,** Одредување на фенолниот профил на претставниците од родот *Teucrium* од флората на Република Македонија со употреба на HPLC-DAD-ESI-MS.

Mitreski Naumče Ilija, Determination of the polyphenolic profile of representatives from the genus *Teucrium* in the flora of the Republic of Macedonia using HPLC-DAD-ESI-MS. (13.12.2012)

ДИПЛОМИРАНИ СТУДЕНТИ

НА ИНСТИТУТОТ ЗА ХЕМИЈА НА ПРИРОДНО-МАТЕМАТИЧКИОТ ФАКУЛТЕТ ПРИ УНИВЕРЗИТЕТОТ СВ. КИРИЛ И МЕТОДИЈ ВО СКОПЈЕ ВО 2012 ГОДИНА

Аналитичка биохемија

Ѓорѓиевска Тоше Надица, 24.1.2012
Алчева Борислав Ана, 3.2.2012
Блажеска Велко Наташа, 10.2.2012
Узунска Ванчо Марија, 15.2.2012
Митрова Томе Билјана, 16.2.2012
Маневска Петре Ивана, 20.2.2012
Тодорова Бранко Кристина, 23.2.2012
Халими Нељми Рабије, 1.3.2012
Сали Зеќир Туљај, 1.3.2012
Божинова Илко Даница, 2.3.2012
Јефтимова Јоце Марија, 2.3.2012
Бужаревски Мирјана Антонио, 6.3.2012
Чапанова Ристо Тања, 16.3.2012
Лазаревска Благоје Анета, 3.4.2012
Бубало Јандре Елена, 22.5.2012
Стојковска Љупчо Емилија, 14.6.2012
Венкова Благојчо Сања, 18.6.2012
Маневска Душко Јована, 29.6.2012
Сибиновска Ѓуре Емилија, 12.7.2012
Јорданова Борис Ирена, 12.7.2013
Соклевска Живко Марија, 12.7.2012
Филдишев Здравко Даворин, 13.7.2012
Дичоска Круме Христина, 30.8.2012
Атанасова Драги Евица 11.9.2012
Кочкоска Војдан Мери, 12.9.2012
Сејфула Исмаил Зејнеп, 14.9.2012
Ефтимовска Гоце Наташа, 14.9.2012
Тушевска Васе Ана, 17.9.2012
Ѓеоргиева Илија Катерина, 19.9.2012
Ѓорѓиевска Илија Магдалена, 27.9.2012
Чанчалова Томе Сандра, 28.9.2012
Дамчевска Методија Душица, 29.10.2012

Применета насока

Гиговски Мирко Мартин, 13.7.2012
Ангеловски Раде Сашо, 14.9.2012
Рајчановска Владо Зорица, 11.9.2012
Трајковска Ванчо Сандра, 9.10.2012

Наставна насока

Ристова Љубе Анета, 28.6.2012
Шурдовски Ѓоко Зоран, 26.9.2012

DOCTORAL THESES

DEFENDED AT THE FACULTY OF TECHNOLOGY AND METALLURGY, Ss. CYRIL AND METHODIUS UNIVERSITY IN SKOPJE, 2012

1

Biljana Anduševa

TRANSFORMATION OF FLY ASH INTO NEW MATERIALS ACCORDING TO THE TETRAD SYNTESIS-STRUCTURE-PROPERTIES-APPLICATION (25.4.2012)

Waste fly ash from REK Bitola, Macedonia ,was used as a raw material for fabrication dense and porous ceramics, composite ceramics and glass ceramics. The waste fly ash and clay were specified from the following aspects: chemical, structural, thermo-chemical, thermo physical and geometrical. Mechanical activation of the raw materials was applied in order to increase the geometrical and the structural factor of the activity.

The consolidation of the ceramics was performed in the temperature interval from 950 °C to 1100 °C/1h with heating rate of 3 and 10 °C/min. The optimization process was conducted based on the influence of the main process parameters and their interactions on the ceramic properties. Density, mechanical properties (E-modulus, bending strength and compressive strength) and the technical coefficient of the thermal expansion were determined on the produced compacts.

The porous structure was created using three types of pore creators, i.e. two types of wood cutting and C-powder. It was confirmed that density, bending strength and E-modulus of thermal treated porous structures shows irreversible dependence on the ratio of the pore creator and linear dependence on the porosity and water absorption.

The concept of multibarier structure was employed to obtain the glass-ceramic composites based on fly ash and waste glass. As a source of liquid phase waste glass was used in quantity from 10 to 50 wt%. The mechanical properties, thermal stability and corrosive resistance of the glass-ceramic composites were specified.

Through a process of vitrification glass ceramics was also produced. The crystallization process for the glass ceramics was determined by defining the glass transition temperature (T_g), exothermic peak of crystallization (T_p), and endothermic peak of melting (T_m). The conversion of amorphous into crystal phases was confirmed by XRD analysis.

It was also confirmed that addition of 5 wt% TiO_2 as nuclei affect the conversion of amorphous to crystal phase as well as mechanical properties of the glass-ceramics.

Keywords: ceramic, glass-ceramic, composite, porous structure, fly ash

2

Dafinka Stoevska-Gogovska

SYNTHESIS AND CHARACTERIZATION OF METAL-METAL OXIDE NANOSTRUCTURED ELECTRODE MATERIALS FOR WATER ELECTROLYSIS (12.5.2012)

The goal in this Ph.D. study was to prepare hypo-hyper d-electrocatalysts (aimed for water splitting) without or with reduced precious metals load and then to characterize them, i.e. to prove whether the goal was fulfilled.

The synthesized electrocatalysts contain metallic (10% wt.) and metal-oxide phase (18% wt.), applied on a carrier (72% wt). The metallic phase was mainly cobalt one, varied from 0%, 50% wt., 80% wt. and 100% (the rest up to 100% wt. being Ru). Only in one case the metallic phase contained 3 different metals, *i.e.* Co, Ru and Pt in a proportion of 80% : 10% : 10%, respectively. Metal oxide phase was TiO_2 (as a crystalline anatase) deposited on a carrier of multiwalled carbon nanotubes (MWCNTs). MWCNTs were pre-activated in 28% nitric acid and effect of the activation process was studied, as well.

As a reference electrocatalyst for hydrogen evolution reaction, corresponding catalyst with metallic phase of pure Pt was prepared.

The prepared electrocatalysts were structurally characterized by means of a number of contemporary experimental techniques. So, by means of X-ray Diffraction Analysis (XRD) the crystal state of each catalyst's phase was determined, and the size of crystal grains was estimated. So, for Pt particles it was found that the size changes from 12 nm, in a systems with Pt as the only metal phase, to 3–4 nm in systems that contain Co (Co:Pt = 1:1 or 4:1). It was determined as well that the anatase particles size in all synthetized catalysts is cca 4 nm.

By means of Photoelectron Microscopy (XPS), the bond energy of catalyst's components was determined, and the extent of interaction was estimated. The components oxidation state was estimated according to their peak amplitude in the XPS spectrum. So, for the carbon the peaks were identified that indicate the existence of double bond (C=C), as well as C-O, C=O (and/or C-OH), -O-C=O and (COO) bonds. The shift of the metallic Ru bond energy was attributed to the existence of hypo-hyper d-interaction between Ru and TiO_2. In some systems the existence of Co(II) was indicated, most probably as $Co(OH)_2$, and of small amount of Co(0).

By means of TEM and SEM microscopic study the shape and size of created particles were determined. So, it was found that the carbon nanotubes diameter is about 20 nm. The existence of interweaved filiform aggregates of MWCNTs with large empty space between them was determined, a phenomenon that does not exists when the carrier is of the traditional Vulcan XC-72 with spherical aggregates and less empty space in between. Except of the inter-particulate porosity, the trans-particulate porosity (along the nanotubes) was identified too.

With infrared spectroscopy (FTIR) it was demonstrated that the difference in the activity of tested materials is not due to the increased hypo-hyper d-interaction, but to other factors, as e.g. the initial intrinsic activity of metallic systems and the size of the metallic phase in the catalysts.

Electrochemical characterization was performed by means of cyclic voltammetry, potentiodynamic method and stationary galvanostatic method in alkaline and PEM hydrogen electrolyser.

The achieved catalytic activity for HER in the alkaline electrolyzer decreased as follows:

Ru > CoRuPt (4:0,5:0,5) > CoRu (1:1) > CoRu (4:1) > Co

In the PEM electrolyzer the rating was some different, i.e.:

CoRuPt (4:0.5:0.5) > CoPt (1:1) > Pt > CoRu (1:1) > Ru > CoRu (4:1)

For OER the rating determined in the PEM electrolyzer was as follows:

CoRu (1:1) > Ru > CoRu (4:1) > Pt > CoRuPt (4:0.5:0.5) > CoPt (1:1).

Keywords: hypo-hyper d-electrocatalysts, TiO_2, multiwalled carbon nanotubes (MWCNTs), hydrogen evolution reaction, oxygen evolution reaction, intrinsic activity, real surface area.

3

Maja Nofitoska

DESIGNING ESTHETICAL AND FUNCTIONAL PROPERTIES AND PRODUCTION OF THE CLOTHING (22.6.2012)

The designing of clothing of required performance, aiming to meet exclusive markets demands, represents a complex process of achieving functional and aesthetic properties of the products, as well as, quality of the clothing assembly processes.

The functional relations of the system, textile structure/performance/ processability are investigated for the range of woven fabrics for outerwear clothing. The fabric parameters and structure variations having influence on investigated clothing performance are defined and functional models are defined.

The influence of sewing machine speed and fabric structure variations on the thread tension, thread consumption and pressure foot displacement is analyzed via on-line monitoring of the stitch forming processes parameters.

The investigations of the garment processability are directed towards enhancement of sewing machine control systems, in order to enhance the capacity of industrial sewing machines to detect sewing defects during sewing operations.

The concept for detecting the incidence of seam pucker in the course of sewing machine operation execution, via monitoring and analysis the values and ratios of specific stitch forming process parameters is suggested.

Keywords: clothing, aesthetics and functional properties, woven fabrics, stitch forming parameters monitoring, seam pucker

4

Ružica Jovanović-Malinovska

NON-DIGESTIBLE OLIGOSACCHARIDES WITH PREBIOTIC CHARACTERISTICS AS NEW COMPONENTS IN FUNCTIONAL FOODS (21.12.2012)

Production and application of non-digestible oligosaccharides with prebiotic characteristics were the main subjects of research in this doctoral thesis. In addition, the consumer acceptance of prebiotics as part of functional foods in Macedonia was assessed.

Detailed data on oligosaccharide type and content present in a wide range of fruits (32) and vegetables (41) grown and commonly consumed in the R. Macedonia were attained. White onion and scallion were found to have relatively high fractions of fructo-oligosaccharides (FOS) and rafinose-family oligosaccharides (RFO), while Jerusalem artichoke, chicory root and garlic distinguished themselves by the highest fructan levels. Most fruits contained low amount of oligosaccharides; the highest content of FOS was found in nectarine. Cluster analysis showed that blueberry, raspberry, watermelon and nectarine from the fruits, and garlic, spring garlic, leek, white onion and scallion from the vegetables formed statistically significant clusters reach in oligosaccharides, thus pointing them as potential sources for commercial extractions of prebiotics.

In the next step, ultrasound assisted extraction was used as a simpler and more effective alternative to conventional extraction method of individual fractions of FOS and RFO from fruits and vegetables which proved to have the highest OS content. Experimental design was performed to determine the optimal conditions for ultrasound extraction (extraction time of 10 min, temperature of 40 °C and 60% ethanol concentration). Ultrasonication not only reduced the extraction time for 83.5% compared with the conventional extraction, it also increased the extracted oligosaccharide content. The highest increase (4.4-fold) of the totally extracted oligosaccharides was observed in Jerusalem artichoke (7.17±0.348 g/100g FW) compared with conventional extraction (1.62±0.094 g/100g FW).

The synthesis of galacto-oligosaccharides (GOS) by β-galactosidase immobilized in both polyvinyl alcohol (PVA) lenses and sol-gel TMOS carriers was studied and compared with the performance of the free enzyme. PVA-immobilized β-galactosidase retained 95% of the initial activity after seven repeated uses and retained 51% of the initial activity after 3-month storage. Lactose conversion occurred at a higher rate in the PVA immobilized β-galactosidase, compared to the immobilized β-galactosidase in sol-gel. Continuous production of GOS from either lactose or whey, with PVA-immobilized β-galactosidase, was performed in a packed-bed reactor. A maximal GOS yield of 30% of the total sugars was attained for a 40 % lactose feed solution with a feed rate of 10.8 ml/h, at pH 4.5 and 40°C, corresponding to a productivity of 117 g/lh. 3-OS and 4-OS were the major types of GOS formed. Conversion of whey in a continuous mode resulted in a GOS production of 15% of the total sugars and formation of 45% 3-OS, 40% 4-OS and 15% 5-OS.

The oligosaccharides were applied for the development of new functional products, a fresh and a processed one. Inulin was incorporated into the fresh quince with vacuum infusion for development of a new functional product that can be consumed as dried quince snack, or as a part of dried energy bar, or muesli formulation. Ultrasonication pre-treatment led to the significant increase in its elasticity and to lower color changes and browning index when compared to the non-treated dried quince. Furthermore, new baked products fortified with oligosaccharides, such as cookies and muffins, were developed. The oligosaccharides used were GOS produced by enzymatic catalysis in this research. The cookies and muffins had good texture and colour characteristics and they were very well accepted by the sensory panel.

A survey based on a web-questionnaire distributed to Macedonian consumers showed their perception, attitude and behavior toward functional foods and prebiotic products. The consumers are willing to buy prebiotic products, although their perception of this kind of products is not clear. They are aware of the effect of healthy nutrition on the human health. Yet, the consumers should be further educated to better understand the exact benefits of functional foods.

Keywords: functional food; prebiotics; non-digestible oligosaccharides; ultrasound extraction; enzymatic production of galacto-oligosaccharides; transglycosilation; food product development

MASTER THESES

DEFENDED AT THE FACULTY OF TECHNOLOGY AND METALLURGY, Ss. CYRIL AND METHODIUS UNIVERSITY IN SKOPJE, 2012

МАГИСТЕРСКИ ТРУДОВИ ОДБРАНЕТИ НА ТЕХНОЛОШКО-МЕТАЛУРШКИОТ ФАКУЛТЕТ ПРИ УНИВЕРЗИТЕТОТ Св. КИРИЛ И МЕТОДИЈ ВО СКОПЈЕ ВО 2012 ГОДИНА

1. **Јанкуловска Цветан Везирка,** Управување со квалитетот на водата во водоснабдителниот систем Студенчица преку имплементирање на интегрална анализа.
   Jankulovska Cvetan Vezirka, Water quality management in the water-supply system Studenčica by integral analysis (17.1.2012)

2. **Шаневска Марија Наташа,** Интегрален модел за проектирање на потсистем за мотивација во системот за управување со квалитет.
   Šaневска Марија Натаša, Integral model for projecting subsystem for motivation in the system of quality management. (12.3.2012)

3. **Петровска Аргил Марија**, Валидација на луминометриската метода за определување на афлатоксините B1 и G1 во зрнеста и добиточна храна.
   Petrovska Argil Marija, Validation of luminometric method for determination of aflatoxin B1 and G1 in seed and silage foods. (23.4.2012)

4. **Ангеловски Анѓеле Горан**, Креирање на интегрален модел за обезбедување на еколошка одржливост на биодизел од аспект на TQM.
   Angelovski Angele Goran, Creation of integral model for providing ecological sustainability of biodiesel based on TQM. (18.5.2012)

5. **Димова Крсте Даниела**, Минимално процесирање на плодови од јапонско јаболко со употреба на јадливи филмови.
   Dimova Krste Daniela, Minimal processing of persimmon with edible coatings. (27.6.2012)

6. **Ганији Исни Арјан,** Сушење на јаболка по осмотски пат.
   Ganiji Isni Arjan, Osmotic of drying apples. (10.7.2012)

7. **Цониќ Момчило Стела,** Моделирање на процесот на сепарација на мирисни компоненти од растително потекло со наткритичен флуид.
   Conić Momčilo Stela, Modeling of the process of separation of fragrance compounds from plant origin by application of a supercritical fluid. (11.7.2012)

8. **Река Агрон Арианит,** Детална карактеризација на природен аморфен SiO_2 од ново лежиште во Р. Македонија.
   Reka Agron Arianit, Detailed characterization of natural amorphous SiO_2 from the new deposit in the R. Macedonia. (9.10.2012)

9. **Ристовски Крсто Божидар,** Карактеризација и функционални својства на протеини изолирани од стабилизирани обезмастени оризови трици.
   Ristovski Krsto Božidar, Characterization and functional properties of proteins isolated from stabilized defatted rice bran. (20.12.2012)

10. **Стефановиќ Стојадин Радмила**, Определување на параметарот ЕБЖ како основа за проектирање на пречистителна станица на индустриските отпадни води во Врање, Р. Србија.
    Stefanović Stojadin Radmila, Determination of p.e.n parameter as a basic stage at industrial wastewater treatment plant design in Vranje, R. Serbia. (24.12.2012)

SPECIALISATION WORKS

COMPLETED AT THE FACULTY OF TECHNOLOGY AND METALLURGY, Ss. CYRIL AND METHODIUS UNIVERSITY IN SKOPJE, 2012

СПЕЦИЈАЛИСТИЧКИ ТРУДОВИ

ОДБРАНЕТИ НА ТЕХНОЛОШКО-МЕТАЛУРШКИОТ ФАКУЛТЕТ ПРИ УНИВЕРЗИТЕТОТ Св. КИРИЛ И МЕТОДИЈ ВО СКОПЈЕ ВО 2012 ГОДИНА

1. **Стојаноска Стојан Марија,** Прехранбени индустриски производи за подобрување на имунитетот кај човекот

Stojanoska Stojan Marija, Industrial food products for immunity boosting effect in humans (09.11.2012)

ДИПЛОМИРАНИ СТУДЕНТИ

НА ТЕХНОЛОШКО-МЕТАЛУРШКИОТ ФАКУЛТЕТ ПРИ УНУВЕРЗИТЕТОТ СВ. КИРИЛ И МЕТОДИЈ ВО СКОПЈЕ ВО 2012 ГОДИНА

Прехранбена технологија

Локвенец Златко Благоја, 9.2.2012
Јовановски Стојча Мартин, 3.7.2012
Марковиќ Катарина, 3.7.2012
Димитровски Винко Дејан, 20.9.2012
Симоновски Томо Милан, 25.9.2012
Јованов Владимир Павле, 26.9.2012
Тренчевски Јордан Стојче, 1.10.2012
Абдуловска Ибрахим Елида, 30.10.2012
Пејчиновска Ѓурѓица Катарина, 28.12.2012

Биотехнологија

Црвенковска Драган Маја, 14.2.2012
Тонева Горан Даниела, 28.5.2012
Насковски Млича Оливера, 11.6.2012
Трајаноска Благон Олгица, 29.6.2012
Сечкова Костадин Магдалена, 3.7.2012
Андонова Петре Билјана, 3.7.2012
Миленковска Спасе Марина, 12.9.2012
Николовска Миле Сања, 18.9.2012
Чонова Ристо Магдалена, 25.9.2012
Атанасова Бранко Надица, 26.9.2012
Петрушевска Зоран Емилија, 26.9.2012
Сарафимова Фердо Александра, 26.9.2012
Милковски Момчило Драган, 28.9.2012
Тодоровски Александар Дарко, 28.9.2012

Конфекциско инженерство

Цветковски Грозде Раде,13.1.2012
Киров Атанас Ристе,13.1.2012
Атанасовска Донче Николина, 31.1.2012
Ѓоргиевска Спасе Катерина,15.2.2012
Милошева Славчо Магдалена,15.2.2012
Хаџи-Јанева Милан Викторија,15.2.2012
Гаштарска Живко Агница,15.2.2012
Ѓорѓиоска Димко Весна, 27.4.2012
Лазаревска Томислав Анѓела, 06.6.2012
Ѓеоргиевски Ѓорѓи Борче,11.6.2012
Цветановска Цанко Ива, 6.7.2012
Јованова Душко Емилија,10.7.2012
Печкова Вано Василка, 5.9.2012
Николовска Драган Марија,30.11.2012

Текстилно инженерство

Мицевска Дионис Христина, 6.7.2012

Дизајн и менаџмент во хемиската индустрија

Јакимовска Страшко Саша, 1.10.2012
Ристовски Михајло Зоран, 7.11.2012

Базно органско и полимерно инженерство

Стојанова Бранко Верица, 15.2.2012
Спасова Крсте Даниела, 3.5.2012
Толовски Толо Митко, 13.6.2012
Фарцаловска Стефан Стефаниа, 22.6.2012
Камов Ќиро Јане, 29.6.2012
Лекоска Спиро Данче, 3.7.2012
Миланова Наунче Ивана, 13.9.2012

Ѓоргиев Атанас Спасе, 17.9.2012

Инженерство за неметали

Анастасова Љубчо Мирјана, 28.5.2012
Гошевска Драган Анита, 1.10.2012

Базно неорганско инженерство

Џелили Шевал Ќатип, 3.7.2012

Преработувачка металургија

Стефановиќ Мирослав Александар, 13.6.2012
Боцевски Борче Гоце, 24.10.2012

Металургија и метални материјали

Петровски Војо Александар, 13.6.2012
Ќимов Никола Дејан, 26.9.2012

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Create and be proud of your deeds
Treasure your love and you'll be loved
Cherish the spirit and be strong

We in Alkaloid, trust in our creations, treasure and cherish the force that sets life in motion and builds perfect harmony called HEALTH.

Health above all

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