Сојуз на хемичарите и технолозите на Македонија

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RIS ALiCE project: Al-rich industrial residues for mineral binders in ESEE region,
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RIS – ALiCE (Project No. 18258):
Al-rich industrial residues for mineral binders in ESEE region

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The growing environmental awareness and need for reducing both the raw material consumption and CO_2 emission of the several industries are recently strongly anchored in various European directives. The Waste Framework Directive (2008/98/EC) in which a waste hierarchy is established gives a high priority to reuse or recycling of materials. The Roadmap to a Resource Efficient Europe (COM 2011, 571) and the Eco-Innovation Action Plan (COM 2011, 899) highly promotes recycling and reuse of waste. In recent years worldwide intensive research efforts are focusing on the development of different types of ecologically sustainable composites which could serve as sustainable alternatives to traditional ceramics.

Generally, the term "Ceramics" is used for inorganic materials made up from non-metallic compounds and made permanent by firing process. The process of production of ceramics is highly energy intensive because it's conducted on temperatures between 800 and 2000 ^{o}C. For example, for porcelain energy account between 10-18 % of the total costs and for bricks energy account between 17-25 % of the total costs.

The success of converting waste materials into ceramic products has been extensively proved in materials such as coal fly ash, metallurgical slags, red mud, marble slurry, construction and demolition waste etc. Fly ash is a residue or by-product of burning pulverized coal in thermal power plants. According to the European statistics for 2016, about 64 % of the total production in EU belongs to the fly ash, of which only 40 % are used, most often in the cement industry as supplements in cement or concrete production. Ceramic is one of the possibilities where significant volume of fly ash can be utilized.

Another efficient way to reduce natural raw materials in ceramics is to partially (or completely) replace it with secondary materials from construction and demolition waste (CDW). According to Eurostat, around 30 % of all waste generated in the EU 27 for 2018 can be associated with CDW, and it consists of various materials such as concrete, bricks, wood, metals, plastic, glass, asbestos, gypsum etc. with recycling levels varying within member states from 10-90 %.

The recycling and re-use of industrial by-products is a huge and complex problem and education, research, discussions and dissemination might contribute to improvement of environmental, economic and social understanding of waste management and open the possibility for production of different products with properties comparable to the ones commercially produced.

Keywords: recycling, re-use, waste, ceramics, fly ash, construction and demolition.

PHYTOCHEMICAL CHARACTERIZATION OF CULINARY *Salvia officinalis* SPECIES

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The medicinal plants have enormous commercial potential throughout the globe. In the herbal boom worldwide, it is estimated that high quality phyto-medicinals will provide safe and effective medication. Many plant species containing active constituents that have a direct pharmacological action on the body. The species *Salvia officinalis* (known as sage) is historically well known from the early 1960s till now by its therapeutic and culinary applications due to its high economic value. The plant is reported to contain alkaloids, triterpenoid, steroids, phenolic compounds and essential oils. Sage plant is a rich source of antioxidant properties, for this reason sage has found increasing application in food industry.

Despite the demand in the food and pharmaceutical industry for methods for fast quality assessment of the herbs and spices, even now there are no official requirements for the minimum content of polyphenols in sage covered by current regulations neither the European Pharmacopoeia monographs nor the ISO 11165 standard. In this work a rapid analytical method for extraction, characterization and quantification of the major polyphenolic and aroma components in sage were developed. Various extractions (infusion; ultrasound-assisted extraction and microwave-assisted extraction) were performed and evaluated for their effectiveness. Identified phenolic compounds were classified as flavone glucosides, hydroxycinnamic acid derivatives, phenolic diterpenes, flavones and flavanones. Rosmarinic acid and its derivatives were dominant component in all analysed samples.

The essential oils content was isolated using Pharmacopoeial hydrodistillation method and analysed with GC/MS method. Identified components were grouped in six different chemical classes: monoterpene hydrocarbons, oxygen-containing monoterpenes, sesquiterpene hydrocarpons, oxygen-containing sesquiterpene, diterpenes and other compounds. Ten components (1,8-cineole, *cis*-thujone, *trans*-thujone, camphor, α-pinene, camphene, β-pinene, myrcene, *trans*-(E)-carophyllene and α-humulene) were present in all sage samples.

Chemical characterized and standardized sage plant material and respective extractive forms further can be utilized for the preparation of appropriate technological formulations for application in the food industry.

Keywords: *Salvia officinalis*, sage, polyphenols, aroma components, essential oils, chromatographic methods.

Acknowledgement: The authors gratefully acknowledge for financial support provided by the Macedonian Ministry of Education and Science for the project titled: "Bioactive compounds of representatives of genus *Salvia* from Macedonia and China: characterization and pharmacological activities", Grant No. 20-6336/2.

PAST BENEFITS-TODAY'S PROBLEMS: CHEMISTRY'S STEERING ROLE IN BALANCING PROGRESS WITH SUSTAINABILITY

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Chemistry has been termed in the 20th century as the central science, mainly due to the key role of physical sciences and applied sciences and because it had a central role in revolutionizing life in general. Few noteworthy examples are the Haber-Bosch process, polymers, manufacturing of electronic devices, metallurgic processes, new materials, but also in terms of planed synthesis of dyes, drugs, agrochemicals etc. In addition, chemists among other scientists were the leading force behind controlling the military-industrial complexes in developed countries (Signatories of Mainau Declaration of 1955 against the use of nuclear weapons and Linus Pauling's work in USA on nuclear disarmament movement and nuclear bomb testing ban). Rational utilization of resources, especially of our carbon mass is a must. The central science has made modern life quite convenient (population boom, increased life expectancy etc.). However everything has come at a price. The current trend of combustion of the bulk of our carbon mass (fossil fuels coal and petroleum) has to be changed. However, in assessment of new resources energy, entropy and environment should not be separated, and short and long-term effects should be weighed in. The industrial processes for obtaining organic and other chemicals were (and some still are) with relatively low yields with many side products, which have not been not properly disposed. Since the global population boom the production of agrochemicals for pest control for essential crops is of utmost importance. The pesticides/insecticides produced in the 20th century have been effective but their biodegradability and selectivity has been quite problematic. One acute problem is the accumulation of persistent organic pollutants (POPs), especially organochlorine pesticides.

Herein we would like to present a case study of the pesticides hexachlorocyclohexanes (HCHs) and their main representative lindane (γ-HCH), which were produced globally including in Macedonia (and Turkey) in the second half of 20th century. Due to their persistence and accumulation in the environment, worldwide efforts have been undertaken for their removal. Our newly formed chromatographic lab at the Institute of Chemistry, PMF, Skopje has been actively involved in assessment, planning and monitoring of the removal of HCHs and corresponding industrial by-products. The chemists especially ones from the academia must take proactive role in these processes of (bulk/trace) removal and remediation of the former dump/industrial sites and subsequent monitoring of the environment (air, water and soil). From our experience in academic labs the standards from industry and commercial laboratories should be implemented and enforced. (Implementation of international standards, ISO 9001, etc. proficiency testing, process of accreditation, standards regarding regular checks of balances, measuring devices, calibration of modern instruments, measuring uncertainties etc.). Even though in academia/universities this is considered time consuming and unnecessary, from our experience it is definitely essential and should be a trend in the 21st century (including training of graduate students). Once this is accomplished the academic scientists can take the leading role in this remediation procedures because they can observe trends and behavior that escapes the eye of analysts and scientists from industrial and commercial sector that do routine analyses. For example, we have noticed that in the environment around the OHIS dump site the relative amounts of epsilon-HCH compared to the original reaction product distribution of the isomers, are much higher. In order for chemists/chemistry to be central or leading science in 21st century, proactive role (involvement) of higher educational institutions is needed-lab accreditation, proper sampling techniques, sample preparation, classical, instrumental analysis, interpretation of result,

suggesting improvement of methods, popularization of science (chemistry) and education of the common public (avoiding spreading panic to the general public). Building network of this kind of academic labs/group with leaders with **high integrity** can give proper unbiased opinion (free of military-industrial complex and other interest groups influence) and which should be included in the decision-making and approval of certain new products or technologies. The new challenges that the 21st century chemists need to tackle are global warming and polyfluoroalkyl substances (PFAS).

PRE-CONSUMER TEXTILE WASTE – CHALLENGES AND POSSIBILITIES FOR NEW PRODUCTS

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The textile industry is a global industry worth $ 2.4 trillion. It is built on a complex and diversified supply chain, including many actors: manufacturers of raw materials, yarns, fabrics and knitwear, finishing, clothing companies, brands, retailers, consumers and disposal / recycling agents. Each stage in the supply chain has the unavoidable side effect of textile waste. By its origin, textile waste can be divided in two broad categories requiring diverse approach in waste management. On one hand, there is the post-consumer or household waste, while on the other, the pre consumer or postindustrial waste generated during the manufacturing process. The division of the clothing supply chain between developed consumer markets and developing countries where apparel production capacities are outsourced, implies that household waste is present in the former countries, whereas the later generates more post-industrial waste.

In the developed world, increasing environmental awareness, as well as social responsibility, reinforced by strict legislations, has led to creating more efficient waste management practices. Still, only 20% of clothing waste is recycled. When it comes to post industrial waste, waste management practices largely depend on the industry. Whereas fibre and yarn waste are largely recycled, apparel manufacturers pay little attention to apparel cutting waste. Furthermore, as textiles are made from natural fibers, chemical fibers or blends divergent strategies of waste management are necessary. Careful sorting by type of fibre is the first step towards reusing or recycling textile waste.

Synthetic fibres, mainly polyester, contribute to 55% of world production of textiles and apparel. The study of technically and economically feasible alternatives for recovery and recycling of these are necessary. For instance, polyester cutting waste can be used as an insulation material for roofing and buildings' internal walls in order to reduce environmental pollution.

Keywords: pre-consumer textile waste, insulation materials

STUDENTS PRESENTATIONS

USING OF FLY ASH FROM FERRO-NICKEL INDUSTRY FOR PREPARATION OF PVC/FY ECO-FRIENDLY COMPOSITES

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Industrial installations, especially pyro-metallurgical plants generate a huge quantity of waste: slags and fine powdery by-product known as fly-ash (FA), recognized as an environmental problem (hot spots). The storage and handling of these waste powders are challenging tasks in the context of environmental impact and sustainable development, as the material is usually disposed on dumps near the plants. The circular economy implies reuse of industrial waste incorporating them in new eco-friendly materials as not expensive equivalents with fulfilled the technical requirements.

The aim of this work is to use flay ash (FA) produced in the first stage of ferro-nickel production in rotary kiln in EURONICKEL, Kavadarci, as reinforcing agent for obtaining PVC-based composites as geomembranes. The composites were prepared by film-casting method using polyvinyl chloride (PVC) matrix reinforced by the FA. FA was applied as as-produced and modified in acid (HCl) and alkaline (NaOH) medium.

FA was characterized by x-ray fluorescence (XRF) method, x-ray diffraction (XRD) method, scanning electron microscope (SEM) and thermogravimetric analysis (TGA). The studied composite systems were characterized by means of scanning electron microscope (SEM), thermogravimetric analysis (TGA) and Fourier-transform infrared spectroscopy (FTIR). Moisture stability was determined by swelling test for 24 h. Corresponding kinetic analysis was done in order to determine adsorption capacity and mechanism of the adsorption process.

The results of the applied techniques have shown well dispersion of the FA particles where the particles were tightly embedded and mechanically interlocked in the PVC matrix indicating strong interfacial interaction with the polymer matrix. The swelling test has shown higher adsorption degree of the composites than PVC, but satisfactory for their use as geomembranes. The composite reinforced with FA previously treated in HCl has shown better adsorption behavior than that previously treated in NaOH.

Keywords: fly ash (FA), ferro-nickel production, PVC/FA composites, geomembrane.

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CIRCULAR ECONOMY IN METALLURGICAL WASTE: APPLICATION OF CONVERTER SLAG FROM FERRO-NICKEL PRODUCTION INTO ECO-FRIENDLY COMPOSITES

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Among the by-products marked as metallurgical waste materials in the ferro-nickel production, converter slag (CS) generates at the last stage of the process – converting. CS contains mainly iron oxides (hematite Fe_2O_3 as the most common one, magnetite Fe_3O_4 and wuestite FeO), MgO, CaO and less SiO_2 and oxides of other heavy metals (Cr, Ni, Co, Zn etc). As such, CS can pose a potential environmental threat to the soil and groundwaters. Following the principles of industrial solid waste management and circular economy, CS can be reused as a low-cost and functional reinforcement in preparation of new eco-friendly composite materials.

The main goal of this study is use of converter slag (CS) from ferro-nickel production in EURONICKEL, Kavadarci, as reinforcement in PVC-based composites. Previously, CS was modified in acid (HCl) and alkaline (NaOH) medium. Further, the treated slag was incorporated in PVC polymer matrix by film-casting method.

The chemical and mineralogical composition of CS, its thermal stability and morphology were studied by means of x-ray fluorescence (XRF) method, x-ray diffraction (XRD) method, thermogravimetric analysis (TGA) and scanning electron microscope (SEM), respectively. Characterization of the prepared composite materials was performed by scanning electron microscope (SEM), thermogravimetric analysis (TGA) and Fourier-transform infrared spectroscopy (FTIR). A swelling test was done in order to determine adsorption behavior of the studied composites.The adsorption capacity and mechanism of the adsorption process, were determined using kinetic model of pseudo-second order.

Keywords: converter slag (CS), ferro-nickel production, PVC/FA composites, geomembrane.

Aknowledgement: This research was supported and performed within the bilateral Project with PR China, "Transformation of industrial waste powders into new functional materials" founded by Ministry of education and science of R. N. Macedonia (No20-6334/1; 29.06.2020).

VARIOUS PROCEDURES FOR PREPARATION OF CERAMIC NANOWIRES

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Due to their unique properties and applications, there is considerably growing interest in synthesis of one-dimensional (1D) nanostructures such as nanowires and nanotubes. Namely, 1D nanomaterials offer the opportunity for investigating the influence of size and dimensionality on their optical, magnetic and electronic properties. Different studies have demonstrated that the incorporation of ceramic nanowires (NWs) in polymer matrix can improve dielectric and energy storage performance. As a ferroelectric ceramic, barium titanate ($BaTiO_3$) nanowires possess a perovskite structure, which exhibits high dielectric constant and low loss characteristics. As a wide-band gap semiconductor with a wurzite structure, zinc oxide (ZnO) nanowires show excellent piezoelectric properties since ZnO has a non-centrosymmetric structure without center of inversion.

The aim of this study is preparation of $BaTiO_3$ and ZnO nanowires using different techniques. A template-free salt-flux-assisted (SFA) method, sol-gel template process and thermal decomposition method were used for synthesis of $BaTiO_3$ and ZnO nanowires. The preparation of $BaTiO_3$ NWs was performed in NaCl-KCl salt flux environment at different temperatures, whereas ZnO NWs synthesized by sol-gel template method were obtained using Polycarbonate (PC) and Anode Aluminium Oxide (AAO) templates. The morphology of the obtained nanowires was analyzed by scanning electron microscopy (SEM) and phase composition was determined by X-ray diffraction (XRD) analysis. The results showed that $BaTiO_3$ NWs have a tetragonal, perovskite structure with no impurity peaks and smooth morphology with few aggregated spherical and quasi-spherical particles. The XRD spectrum of the ZnO NWs reveals that all diffraction peaks can be indexed to the hexagonal wurzite structure, with no impurity peaks. In addition, SEM images showed that ZnO NWs were mostly parallel to each other, with length less than 12μm. Future work is still in progress to optimize the preparation of ZnO NWs, in order to improve their aspect ratio.

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Keywords: 1D nanostructures, nanowires, $BaTiO_3$, ZnO, SEM, XRD

Hg - MERCURY ANALYSIS OF AL-RICH INDUSTRIAL RESIDUES FOR MINERAL BINDERS IN ESEE REGION

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Mercury is released into the environment by humans during various activities, e.g. the burning of fossil fuels, alternative fuels and waste materials such as old tyres, and in the production of cement and some metals, such as gold. Is a highly toxic, naturally occurring metal that causes significant harm to both human and ecosystem health. Due to the toxicity of the mercury, EU has strict regulations that needs to be used as Best Available Techniques for reducing emissions of mercury to the environment. For production of cement, lime and magnesium oxide, companies should select materials with a low content of mercury, and limit the content of relevant metals in materials, especially mercury. The BAT emission levels for mercury from the flue-gases of kiln firing processes should be no higher than 0.05 mg/Nm^3.

"RIS-ALiCE" project aims on the recycling and material chain optimization for End-of-Life products.The main goal of the "RIS-ALiCE" project is to create a network of relevant stakeholders, in the area of currently unused and landfilled Al-rich industrial residues and to increase the innovation potential and competitiveness of the East and South East European (ESEE) region. During the project "RIS-Alice" were analyzed and mapped secondary materials that could potentially be used in the cement industry to produce new types of clinker, or low CO_2 clinkers/cements. In addition to all the characteristics of the secondary materials, concentration of mercury was also analyzed, according to the EU regulations if the secondary raw materials are suitable for reusage in cement industry. Atomic absorption spectrometer AMA-254 (Advanced Mercury Analyzer) with direct solid sampling was used for determination of mercury.

The AMA254 Advanced Mercury Analyzer is a unique Atomic Absorption Spectrometer that is specifically designed to determine total mercury content in various solids and liquids—without sample pre-treatment or sample pre concentration. Designed with a front-end combustion tube that is ideal for the decomposition of difficult matrices like coal, combustion residues, soils, and fish, the instrument's operation may be separated into three phases during any given analysis: Decomposition, Collection, and Detection

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Keywords: Mercury, environment, clinker, Portland cement

SUSTAINABLE MATERIALS IN METALLURGY – INCORPORATION OF FERRO-NICKEL METALLURGICAL SLAG IN PVC-BASED COMPOSITES

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Ferro-nickel production industry in EURONICKEL, Kavadarci generates more than 1 Mt slag from the electric-arc furnace (EAFS) during the reductive smelting of ferro-nickel. Traditional disposal of this type of waste in dumps can be potential environmental risk for the soils and groundwaters. According to the principles of the circular economy and sustainable development (reuse instead of disposal), this type of material can be incorporate into polymers, as non-expensive and effective reinforcing agent, forming new sustainable and eco-friendly composite materials.

This study is concerned with use of electric-arc furnace slag (EAFS) produced in the second (the main) stage of ferro-nickel production in EURONICKEL, Kavadarci, as reinforcing agent for preparing PVC-based composites. The composites were prepared by film-casting method using polyvinyl chloride (PVC) matrix reinforced by the EAFS. Previously, EAFS was treated in acid (HCl) and alkaline (NaOH) medium.

X-ray fluorescence (XRF) method, x-ray diffraction (XRD) method, scanning electron microscope (SEM) and thermogravimetric analysis (TGA) were used to characterize the EAFS. The prepared composite samples were studied by means of scanning electron microscope (SEM), thermogravimetric analysis (TGA) and Fourier-transform infrared spectroscopy (FTIR). Water resistance was tested by immersing the samples into water for 24 h, measuring the water yield in corresponding time intervals. Adsorption capacity and mechanism of the adsorption process were determined using the model of pseudo-second order.

The obtained results highlight well dispersion of the FA particles where the particles were tightly embedded and mechanically interlocked in the PVC matrix indicating interfacial interaction with the polymer matrix. Water resistance test has shown higher adsorption degree of the composites than PVC, but satisfactory for their use as geomembranes. Comparing the composites with different treated EAFS, one can conclude that the composites containing EAFS previously treated in HCl has shown better adsorption behavior than that treated in NaOH.

Keywords: electric-arc furnace slag (EAFS), ferro-nickel production, PVC/EAFC composites, geomembrane.

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RADIOLOGICAL ANALYSIS OF AL-RICH INDUSTRIAL RESIDUES

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Naturally occurring radioactive materials (NORM) are present in almost every location and regarding their amount and utilization, radiological problems can be caused. Significant challenges for reuse of NORM can be connected with: uncontrolled migration of radioactive materials from waste in the environment and important urge of low-cost raw materials in European industries. Primordial radionuclides, members of the uranium (^{238}U, ^{235}U) and thorium (^{232}Th) radioactive chains, and the potassium isotope ^{40}K can be found as main constituents of a rock or as trace elements [1].Bauxite residue and fly ash are industrial waste that is generated on a massive scale. Red mud or bauxite residue is a product of the Bayer process during the production of alumina and it is a complex material with various chemical and mineralogical composition [2]. Fly ash is a fine powder that is a byproduct of burning pulverized coal in electric generation power plants [3]. In addition, geopolymers are the emerging class of materials with remarkable properties. They are obtained by reaction of aluminosilicate-rich precursor (metakaolin, red mud, fly ash etc.) and an alkaline activated solution (alkali hydroxides, oxides, carbonates etc.), resulting in an aluminosilicate network structure which contributes to maintaining excellent properties (resistance to extreme temperatures and corrosion and compressive strength) [4]. Some of the potential uses of these Al-rich residues can come in forms of recovery of major or minor constituents and direct uses or incorporation into building materials, medicine, automobile composites etc. In order to assess the possibility of usage of these materials in building industry the radiological analysis needs to be performed. It is most often performed by gamma ray spectrometry with a semiconductor high purity germanium (HPGe) detector. Application of this method gives qualitative and quantitative characterization of radionuclide content (activity concentrations) in investigated material [5]. Therefore, in this research a radiological characterization of Al-rich residues was performed and gamma emitting radionuclides were analyzed to determine the radiological impact and their suitability for potential applications. Obtained results of ^{226}Ra, ^{232}Th, ^{40}K activity concentration and performed calculations of activity concentration index (ACI) and dose assessment (radium equivalent activity (Ra_{eq}), external hazards index (*Hex*), the external absorbed dose rate (*D*) and annual effective dose rate (*EDR*)) clearly prove that investigated samples of fly ash and geopolymer are suitable for utilization in construction industry as building material or its constituent with no restriction. Contrary, for red mud sample ACI value is above the recommended value – 1 mSv per year and its utilization needs to be restricted in terms of its mass fraction in the final product of building material.

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Keywords: red mud, fly ash, geopolymer, gamma-ray spectrometry

CRITICAL RAW MATERIALS (CRMs) IN BAUXITES – THE SLOVENIAN CASE STUDY

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Bauxite, white to reddish-brown residual sedimentary rock formed by lateritic weathering of the aluminosilicate minerals within the parent rocks, is not only the most important aluminum ore, but also an important source of several critical raw materials (CRMs) [1] including Ga, Sc, V, Ti and rare earth elements (REE). On the territory of Slovenia more than 40 bauxite deposits have been explored. However, levels of CRMs in them remained unknown.In scope of the RIS-ALiCE project, which valorizes potential sources of alumina for the new generation of the cement clinkers, bulk bauxite samples were collected from Triassic (Podlipa), Jurassic (Hrušica-Nadrt), Cretaceous (Nanos-Železni Klanci and Hrast pri Vinici) and Oligocene (Kokarje-Žifernik) stratigraphic horizons within Slovenia.X-ray fluorescence spectroscopy (XRF) and inductively coupled plasma optical emission spectrometry/mass spectroscopy (ICP OES/ MS) chemical analyses on samples fused with Li metaborate enabled almost complete digestion of the material and analyses of major, minor and elements, including many CRMs.

On average analyzed samples contains 389 ppm LREE, 136 ppm HREE, 61 ppm Ga, 37 ppm Sc, 234 ppm V and 2,8 % TiO_2 respectively. Detected CRM levels are comparable to the CRM levels in Greek bauxites [2] and lower in comparison to the bauxites in Montenegro [3]. Detected levels of the CRMs varied between bauxites of the different ages. The highest levels of LREE, HREE, Sc and Ga were detected in Triassic bauxites amounted on 511 ppm, 199 ppm, 43 ppm and 69 ppm respectively, while Jurassic bauxite contains the highest levels of TiO_2 – 2,8 % and Cretaceous bauxites contain the highest levels of V – 428 ppm. Results show that bauxites in Slovenia contains elevated levels of Ga, Sc, V, Ti and REE. However, the potential for the exploitation of analyzed bauxites is limited by a relatively high presence of SiO_2 (average level 13.4%) and small dimensions of the deposits.

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Keywords: bauxites, critical raw materials, ICP OES/MS, REE, XRF

EFFECT OF TEMPERATURE ON PHASE ASSEMBLAGE OF BELITE CALCIUM-SULFOALUMINATE CEMENT

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Belite-calcium sulfoaluminate cements are alternative cements to ordinary Portland cement, as they require less energy and produce a lower amount of carbon dioxide during their production [1]. Temperature is known to alter the hydration of cement materials, as well as their physico-mechanical properties [2,3]. Aim of the study was to investigate the influence of different curing temperatures on the hydrated phase assemblage of belite calcium-sulfoaluminate cements.

For that purpose, cement clinker was synthesized with targeted phase composition to obtain the targeted amounts of belite (C_2S), calcium sulfoaluminate ($C_4A_3\overline{S}$) and ferrite (C_4AF). To prepare the cement, gypsum was added to ground clinker based on defined calcium sulfate to calcium sulfoaluminate molar ratio. The hydration process was investigated at 5, 20, 40 and 60 °C during different curing periods. The phase assemblage of hydrated cements (i.e. type and amount of phases) was studied by thermogravimetric analysis (TGA), X-ray powder diffraction (XRD) and Rietveld refinement. In addition, microstructure of cement pastes and detailed chemical composition of hydration products was studied by scanning electron microscopy with Energy dispersive X-ray spectroscopy (SEM/EDS). Results of the experimental part were compared to a thermodynamic model established using the geochemical modelling program GEMS and thermodynamic database CEMDATA18.

The results showed that curing temperature significantly affects the type and amount of precipitated hydration products. As evidenced by X-ray diffraction and thermogravimetric analysis, during the hydration, the anhydrous clinker phases were consumed and hydration products such as ettringite, monosulfate, strätlingite and siliceous hydrogarnet were formed, in addition to the amorphous phases. Scanning electron microscopy results confirmed those findings and showed that the chemical composition of hydrate phases is also altered by curing temperature. The calculated thermodynamic model showed a good agreement with experimental data.

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Keywords: temperature, belite-calcium sulfoaluminate cement, hydration.

DETERMINATION OF SELENIUM IN HUMAN PLASMA AND BLOOD BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY (ETAAS)

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Selenium in form of selenomethionine and selenocysteine, is an integral part of the active center of glutathione peroxidase, thioredoxin reductase and iodotyronine deiodinase which have antioxidant activity and plays an important role in the metabolism of thyroid hormones [1]. Therefore, blood selenium concentration is strongly correlated with immune function, thyroid disease and tumourigenesis [2]. Due to the importance of monitoring the concentration of selenium in the blood, a method for determination of selenium in the blood and plasma by electrothermal atomic absorption spectrometry (ETAAS), has been optimized.

The proposed method is simple, rapid, accurate and suitable for routine clinical analysis. The samples of blood and plasma were prepared by their dilution in ratio of 1+2 with 0.2% detergent solution (Triton X-100, Tween 80 and SDS) and 0.1% nitric acid solution. It was found that Pd modifier should be applied with the optimal pyrolysis temperature of 1100ºC for 30 s for plasma and 35 s for blood and optimal atomizing temperature of 2500ºC.

The method was applied for determination of Se in plasma and whole blood samples of 57 healthy volunteers (31 female and 26 male) with average age of 47 years. Health status was estimated by blood test which includes complete blood count (CBC), biochemical parameters and thyroid status.The results obtained revealed that the selenium content varied in the range of 31.40–47.01 μg/L. No significant difference has been revealed between women 38.84±4.23 (31.40-47.01) μg/L and men 40.43 ± 3.62 (34.02-46.70) μg/L. These results are in relatively narrow range of values compared to the results of previous reports [3], probably due to including criteria for chosen healthy individuals. The concentration of selenium in whole blood is higher by 23-25% in all samples due to distribution of selenoproteins in plasma and blood cells. Our data reveal that plasma selenium level of healthy people in Macedonia is among the lowest in Europe, but comparable with those in Balkan region.

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Keywords: selenium, blood, plasma, electrothermal atomic absorption spectrometry

DETERMINATION OF MAJOR AND TRACE ELEMENTS IN THE PLANT *SEDUM OCHROLEUCUM* AND SERPENTINE SOIL IN LLAPUSHNIK, KOSOVO

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The objective of this study was the determination of major and trace metals (K, Ca, Mg, Fe, Na, Mn, Ni, Cu, Cd, Cr, Pb and Zn) in the plant species *Sedum ochroleucum*, the plant which grown in serpentine soils in the Llapushnik mountains. The serpentine areas located in the Balkan Peninsula are widespread and form a belt from Bosnia to Greece [1].

Five subsamples were collected in an area 50x50 m^2, the plant samples were put in paper bags of 1 L and the soil samples of 1 kg in plastic bags. The plant samples were separated in three parts: root, stem, and leaf, they were prepared in a standard procedure of cleaning, drying, and digested in the microwave digestion system. The plant samples and soil samples were analyzed by Flame atomic absorption spectroscopy (FAAS).

The concentration of metals (in mg/kg) in soil samples decreased in order: 66440 (Mg) > 61338 (Fe) > 5134 (Ca) > 3366 (Cr) > 3289 (K) > 2869 (Mn) > 2700 (Ni) > 996 (Na) > 236 (Zn) > 138 (Pb) > 24.7 (Cu), and cadmium was below limit detection. The ratio Mg/Ca was 13 and the content of metals were similarly with results of other authors presented for serpentine soils investigated [2,3]. The content of potassium and calcium in plants' leaves was higher than in soil sample, so the BCF values were 1.2 and 1.4 respectively. The results show that TF values for root to leaf translocation was higher than 1 for four metals: calcium-2.4; zinc-1.5; copper-1.2, and 1.1 for magnesium.

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Keywords: *Sedum ochroleucum,* serpentine soil, metals, FAAS, Kosovo

CONCENTRATION OF SOME METALS IN THE ENDEMIC PLANT SPECIES *STACHYS SCARDICA* AND SERPENTINE SOIL IN GOLESH, KOSOVO

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The largest serpentine soils in Europe occur in Balkan Peninsula, and Kosovo as a part of this region has an ultramafic area of 487 km^2 in its territory [1]. The aim of this study was the determination of some metals (K, Ca, Mg, Fe, Na, Mn, Ni, Cu, Cd, Cr, Pb and Zn) in the plant *Stachys scardica*, as an endemic plant species which grown in serpentine soils in the mountains of Golesh.

To perform this study, five subsamples were collected in an area 50x50 m^2, the plant samples were put in paper bags of 1 L and the soil ones of 1 kg were put in plastic bags. Three main parts of the plants were taken for analysis: root, stem, and leaf. They were prepared in a standard procedure involving cleaning, drying. Further they were digested in the microwave digestion system, and the metals' content was measured by a flame atomic absorption spectroscopy spectrometer (FAAS).

The concentration of metals (in mg/kg) in soil samples decreased in order: 53939 (Mg) > 49647 (Fe) > 7448 (Ca) > 2813 (Mn) > 2580 (Ni) > 1773 (K) > 1297 (Cr) > 958 (Na) > 138 (Zn) > 90.2 (Pb) > 26.2 (Cu), and cadmium was below limit detection. The ratio Mg/Ca was 7.2 and the content of metals were similarly with results of other authors presented for serpentine soils investigated [2,3]. The BCF values for potassium were from 1.5 to 2.4, and for other elements these values were less than one. The translocation factor (TF) values for calcium and magnesium by root to leaf transfer were 2.9 and 2.3 respectively.

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Keywords: *Stachys scardica*, serpentine soil, metals, FAAS, Kosovo

IDENTIFICATION OF PYRROLIZIDINE ALKALOIDS IN BORAGINACEAE SPECIES FROM NORTH MACEDONIA

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Pyrrolizidine alkaloids (PAs) are a group of secondary metabolites produced by plants all over the world as a defense mechanism against herbivores. Over 660 PAs and their corresponding N-oxide derivatives have been identified from more than 6000 plant species. PAs have been reported to be hepatotoxic, mutagenic, and carcinogenic to both livestock and humans. The occurrence in plant world is scattered in several botanic families with special abundance in Asteraceae, Boraginaceae and Fabaceae. In North Macedonia, only the species from Boraginaceae and Asteraceae family have been reported.

The aim of this study is to assess the presence of PAs in three plant species, *Echium vulgare*, *Onosma heterophyllum*, and *Cynoglossum creticum*, all from the Boraginaceae family. For this purpose, plant samples were collected from 10 locations from different parts of North Macedonia. The plants were investigated for PAs by methanolic extraction followed by HPLC/MS analysis.

The results of the analysis show presence of several PAs, mainly from retronecine and heliotridine structural type (Figure 1). In particular, the following PAs from retronecine type were detected: echiuplatine, asperumine, lycopsamine-*N*-oxide or intermedine-*N*-oxide, derivative of retronecine. Three PAs from the heliotridine type were qualitatively identified: heliotrine, heliotrine-*N*-oxide, europine-*N*-oxide. Additionally, a derivative of (+) – trachelanthic acid was detected.

Given this, in future studies, the plants of this family should be further screened for determinations of PAs quantitatively and for identification of new PAs.

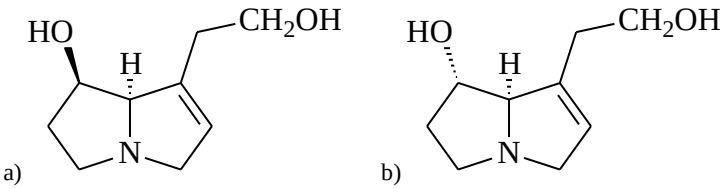

Figure 1. Chemical structure of a) retronecine and b) heliotridine

Keywords: pyrrolizidine alkaloids, Boraginaceae, HPLC, mass spectrometry

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VALIDATION OF GC/ECD AND GC/MS METHODS FOR ANALYSIS OF ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS IN SOIL

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Polychlorinated biphenyls and organochlorine pesticides are organic pollutants resistant to degradation which contribute to environmental contamination. These organochlorine compounds have a wide range of acute and chronic health effects, including cancer, neurological damage, reproductive disorders, immune suppression, birth defects, and are also suspected endocrine disruptors [1]. Soil is dynamic, living, natural body that plays many key roles in terrestrial ecosystems [2]. Plants absorb the residues of pesticides in soil. That way POPs enter the food chain and bioaccumulate. Years after the worlds ban since the Stockholm Convention in 2001 for production and use of PCBs and OCPs, these chemicals can still be found in many areas in different parts of the world [3].

The goal of this study is verification of a standard EPA method for analysis of 24 PCBs and OCPs in soil samples [4]. The method verification implies examination of the extraction procedure efficiency, as well as the analytical method. For this purpose, analysis of uncontaminated soil samples spiked with a mixture of seven polychlorinated biphenyls (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180) and seventeen organochlorine pesticides (hexachlorobenzene, α – HCH, β – HCH, γ -HCH, aldrin, dieldrin, endrin, heptachlor, heptachlor epoxide (*cis*- and *trans*-), α – endosulfan, *p, p'* – DDE, *o, p'* – DDD, *o, p'* – DDT, *p, p'* – DDD, *o, p'* – DDE and *p, p'* – DDT) was validated. The analysis was performed by GC/ECD, furthered by GC/MS for identification. The optimized method used during the analysis, involves splitless injection with mobile gas gradient with temperatures from 80 to 295 °C in the oven, and 350 °C as the detector temperature. Nitrogen is used as makeup gas. The column is 30 m × 0,25 mm × 0,25 µm with HP – 5 as stationary phase.

Six different soil samples were analyzed by three analysts. They were spiked on two concentration levels, 20 µg/L and 120 µg/L, three of each. The evaluated parameters include relative retention time, repeatability of relative retention time, repeatability of peak height, linearity, sensitivity (LOD and LOQ) and relative peak height. The final results are expressed as mass of a polychlorinated pesticide in µg in 1 kg of soil [4]. Better results were observed from the higher concentration level of spiked samples with the standard PCB and OCP mixture. The total calculated recovery is 93,2 % with RSD 9,1.

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Keywords: Polychlorinated biphenyls, Organochlorine pesticides, soil, GC/ECD, GC/MS.

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DEVELOPMENT OF ANALYTICAL METHODS FOR EXTRACTION AND CHARACTERIZATION OF PYRROLIZIDINE ALKALOIDS IN PLANT MATERIAL

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Among naturally occurring plant constituents, the 1,2-unsaturated pyrrolizidine alkaloids (PAs) play a distinct role because of the large number of congeners occurring in nature and the pronounced toxicity of some of them. PAs are distributed in plant families of *Asteraceae*, *Boraginaceae*, *Fabaceae*, *Orchidaceae* and *Apocynaceae* and serve in the chemical defense mechanism against herbivores [1]. The content of PAs in plant materials and food products can vary from trace to very high levels and it was found that the difference of PA content significantly depends on plant type, but also on the nature of the solvent and the applied extraction technique. Therefore, appropriate analytical methods for extraction and determination are needed [2].

In our study, systematic examination of the extraction efficiency of PAs using 17 available standards was carried out using 15 different solvent mixtures containing methanol, ethanol or water with or without formic, sulfuric or hydrochloric acid. High-performance liquid chromatography coupled to mass spectrometry (HPLC-MS) was used for separation and identification of pyrrolizidine alkaloids and their *N*-oxides because of its selectivity and sensitivity. The extraction solvent composition was found to have a significant effect on the yield of total as well as specific PAs. Pure methanol was found to be the most efficient solvent compared to all the other ones tested.

The developed method was successfully applied for characterization of PAs in extracts prepared from different parts of cultivated *Symphitum officinale* commonly known as comfrey. The following PAs were found in the samples: lycopsamine, lycopsamine-*N*-oxide, 7-acetyllycopsamine, 7-acetylintermedine and echimidine.

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Keywords: Pyrrolizidine alkaloids, extraction, *N*-oxides, plant material, HPLC-MS

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DEVELOPMENT OF A REVERSED-PHASE ION-PAIR HPLC METHOD FOR DETERMINATION OF NITRATES AND NITRITES IN GROUNDWATER AND BOTTLED WATER SAMPLES

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Nitrates and nitrites are found in groundwater because of the increasing use of artificial fertilizers, disposal of wastes (particularly from animal farming) and changes in land use [1]. Their presence in low amounts is desirable for the growth and development of living organisms but at concentrations exceeding safe levels, these compounds pose a wide variety of health risks. Therefore, it is necessary to determine and monitor their levels in water, sewage and food. There are many published methods for determination of nitrates and nitrites, based on their derivatization using the Griess reaction in which they form azo dyes that can be quantified using UV-Vis spectrophotometry. Other group of methods use ion-exchange liquid chromatography methods and reversed-phase ion-pair HPLC methods but are more complex and often lack experimental information when it comes to reproducing the method [2].

In this work, a simple, accurate and sensitive method was developed and validated for simultaneous determination of nitrite and nitrate in groundwater and bottled water using reversed-phase ion-pair HPLC without the need for pre-column derivatization. Separations were accomplished in 30 minutes using a reversed-phase C_{18} column (250 mm x 4 mm i.d., 5 µm particle size) with a mobile phase containing 85% 5.0 mM ion-pair reagent tetrabutylammonium hydroxide set to pH 2.5 using sulfuric acid and 15% acetonitrile (flow rate 1.000 mL/min). UV absorption measured at 222 nm showed linear response over a wide concentration range from 0.10 to 20.0 mg/L for both anions. The detection limit was 0.02 mg/L, and quantification limit was 0.05 mg/L for both anions. The method was validated and demonstrated as reliable for its purpose. It was then applied for analysis of nitrates and nitrites in different water samples. Nitrites were not detected in groundwater and bottled water as their concentration was below the detection limit. Concentration of nitrates in bottled water ranged between 0.3 mg/L and 7.7 mg/L, and in groundwater samples their concentration ranged between 4.4 mg/L and 19.9 mg/L.

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Keywords: Nitrates, nitrites, HPLC, ion-pair, groundwater, bottled water

DISTRIBUTION AND STATISTICAL ANALYSIS OF MAJOR AND TRACE ELEMENTS IN THE BEE POLLEN FROM THE WHOLE TERRITORY OF REPUBLIC OF KOSOVO

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The objective of this study was determination of major and trace elements in the bee pollen samples from the whole territory of Republic of Kosovo. Bee pollen is known as a natural superfood due to its indispensable nutritional and medicinal properties [1]. Pollen, as a natural plant product, is exposed to different contaminations absorbed by plants from the soil through root system or with water intake, as well as to numerous pollutants of different origin, including anthropogenic ones, deposited directly on pollen [2]. The geology of Kosovo is complex, with formations created at different intervals of geology timeline, there is also a high mineral activity of Pb-Zn, Cu, Ni and Cr positioned in different parts of the territory [3].

In total 67 pollen samples were collected during June-August 2019 and digested in a microwave digestion system. The samples were analyzed for 27 macro and microelements by using ICP-AES and ICP-MS. The mean content of major elements in bee pollen were: 4065, 3455, 1375 and 549 mg/kg for K, P, Ca and Mg, respectively. The contents of potassium and phosphorus were in higher than in pollen from Turkey and Serbia, but the contents of calcium and magnesium were lower than in the bee pollen from Serbia [4, 5]. The range of the contents for some potentially toxic elements were: 11.9-139.1, 1.9-16, 0.11-6.25, 0.01-0.329 and 0.001-0.38 mg/kg for Zn, Cu, Pb, Cd and As, respectively. The maximum content for zinc and lead was higher, for copper similar, and for arsenic was lower than in the bee pollen from Turkey [6]. The distribution maps of elements analyzed, and the statistical analysis were used to explain the correlation between the chemical elements, the groups of elements and their lithogenic or anthropogenic origin.

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Keywords: Bee pollen, major and trace elements, lithogenic, anthropogenic, Kosovo

DETERMINATION OF STORAGE CONDITIONS FOR GRAPE POMACE BISCUITS USING THEIR SORPTION ISOTHERMS

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One of the biggest challenges today is the use of waste from the food industry as a raw material for new products, all in order to protect the environment from pollution. In this research,functional biscuits were produced, containing grape skin, stalk and seeds, obtained as a by-product from the wine industry. Functional biscuits represent healthier alternative of the usual biscuits, due to the large amount of dietary fibers occurring in the used by-product. This research aims to determine the sorption isotherms of newly created functional biscuits with incorporated grape waste as a way to determine their stability. 12 different formulationswere producedconsisting of 3 different granulations of grape pomace (0.25, 0.50, 1.00mm) replacing thewheatflour in 4 different percentages: 2.5%, 5.0%, 7.5%,and 10.0% (w/w). The equilibrium between the sample and the atmosphere was achieved by placing the samples in desiccators holding different concentrations of sulfuric acid for attaining different relative humidity of the atmosphere (aw = 0.971; 0.750; 0.642; 0.513; 0.318; 0.171) at room temperature for 17 days until the balance was reached. The obtained results were further used to obtain sorption isotherms.The sorption isotherms are plotted as sinusoidal functions giving the ratio of moisture absorption and desorption in each of the biscuits. This relationship is complex and unique to each biscuit. In agreement to the classification of sorption isotherms according to their shape, 5 different types are known. Therefore, the sorption isotherm for the reference biscuits corresponds to the type 4 sinusoidal curve.In this category also belong biscuits nriched with a grape pomace content of 5.0%(w/w) and 10.0%(w/w)in granulation of 1 mm. The sorption isotherm for the biscuits in which 1mm granulation was used, in quantity of 2.5% (w/w) corresponds to the sinusoidal curve of type 2, while the sorption isotherm for the biscuit in which the wheat flour was replaced by grape pomace in 7.5% (w/w) from the same granulation, corresponds to the type 5 sinusoidal curve.

Sorption isotherms presenta good tool for predicting the shelf life of functional biscuits. From the obtained results it can be concluded that the most stable and close to the stability of the controlbiscuits are those made with 10.0% (w/w)grape pomace as substitution of the wheat flour in granulation 1 mm, indicating good shelf life in combination with suitable packaging.

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Keywords: by-product, functional biscuits, grape pomace, shelf-life, sorption isotherms

THE EFFECTS OF GRAPE POWDER INCLUSION ON THE PHYSICAL PROPERTIES OF MUFFINS

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One of the main trend nowadays is the production of high quality food. Researchers' work is moving in the direction of creating composite flours, containing wheat but also some amount of flour made from other grains, fruits or vegetables. The goal of using composite flours is to improve the nutritional value of cereal containing products. There is a growing interest for valorisation of by-products generated within the food industry. Winemaking industry is producing a large quantity of grape skin, stalk and seeds, which contain bioactive compounds (polyphenols, anthocyanins, and flavonoids), dietary fibres, free monoterpenes, and moreover they are available at low prices. This by-product in a form of powder can be a partial substitution of the wheat flour without changing the calorie value of the product. Muffins are sweet bakery desserts that are relatively easy to make and are consumer favourites because of their fine taste and soft texture, however they cannot be categorized as a healthy snack. The aim of this research is to determine the impact of different concentrations (2.5, 5.0, 7.5, 10.0 and 15.0 %, w/w) of grape skin, stalk and seed flour, as a replacement of conventional flour in a muffin recipe, considering the physical characteristics (dimensions and colour) of this functional food. The new muffin formulations were compared with a referent recipe, in which only wheat flour was used. For determining the stability and qualitative changes, batch of muffins were placed in a metalized polyethylene package and were stored 7 and 15 days, respectively. It was observed that the diameter, height, mass and the porosity have increased by gradual increasing of the concentration of grape skin, stalk and seeds in the freshly baked muffins. This result occurs due to the higher bulk density of the grape flour in comparison to the wheat flour. The water content decreased as the addition of grape flour percentage increased, while the water activity did not change. The colour of the muffins has generally turned darker, the red tone has increased however the yellow tone has decreased. During the storage period, the dimensions of the muffins have changed. A decrease in mass, diameter and volume has been observed in all recipes due to the release of water that causes the product to shrink. Moreover, moisture evaporation was also confirmed by the reduced water content in the muffins during storage. However, the addition of grape skins and seeds in powder to muffins resulted in a slightly reduced initial moisture, while water activity did not change. The porosity of the material decreased over time due to the increase in crumbliness.

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Keywords: by-products, functional muffins, grape husk and seeds, physical properties

INULIN EXTRACTION FROM ONION AND LEEK

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Inulin is a water-soluble polysaccharide that can be found in many different plants, fruits and vegetables like banana, garlic, onion, leek, chicory root, Jerusalem artichoke etc. Inulin consists of fructose units with one glucose unit as a terminal molecule. The fructose units are linked by β(2—1) bonds. The glucose molecule, at the end of each fructose chain, is linked by an α(1—2) bond. Inulin is used to modify texture, replace fat, or as a low-calorie sweetener [1]. It is considered as prebiotic because it improves the growth of beneficial bacteria in the human gut while it suppresses the proliferation of the pathogenic microorganisms. Therefore it can be used as a supplement against colon cancer, high cholesterol concentrations, and improves mineral absorption [2, 3].

Different extraction methods were analysed for inulin extraction from *Allium cepa* (onion bulb) and *Allium ampeloprasum* (leek stalk). The conventional method of extraction, and ultrasound and microwave assisted extraction were used by testing the effect of the extraction time on the yield. Three level matrices were created to plan the experiments. All experiments used distilled water as a solvent and the solid-liquid ratio was 1:10. Results showed that all methods of extraction give satisfactory yield of inulin.

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Keywords: inulin, extraction, onion, leek.

PRODUCTION OF SHORTBREAD COOKIES WITH NON-CONVENTIONAL METHOD USING FAT MIMETICS

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The huge increase in the number of people suffering from diabetes, obesity, viruses, cancer, countless chronic diseases and many other complications on human health are reminding us every day that it is time to change some of the daily eating habits. It is necessary to increase the general awareness of people that it is in the common interest to increase and strengthen immunity, which can be achieved through more frequent consumption of healthy food. Eating healthy food would facilitate the work of our body, because it receives all the necessary nutrients, and to thank us, it "gives" us the energy we need to perform daily responsibilities and as a bonus our body is ready to fight some diseases. Today we live surrounded by many modern technologies that improve production of food products and just with a small innovative change they can be produced alternatively and be rich in nutrients at the same time, yet minimally different from conventional food products [1].

The aim of this research was to produce healthy short bread cookies low in fat by using fat replacement. Instead of conventional fat, such as butter, an emulsion that contains a functional component inulin was produced by sonication. Inulin does not break down until it reaches the large intestine, where it acts as a prebiotic, feeding the "good" bacteria. With this emulsion, two goals were achieved: first elimination of trans fatty acids that raise the "bad" cholesterol in blood, resulting in huge complications and diseases in humans, and the second goal that was achieved is the (increased) intake of inulin.

For this purpose, three different types of cookies have been made [2]. First group was with butter and it was used as a reference. The second group was prepared with 50% replacement of the butter, while the third group was with complete replacement of the butter with the inulin emulsion. The emulsion consisted of inulin and extra virgin olive oil. From the results it was concluded that the characteristics of the short bread cookies did not differ too much between the recipes. Small differences in the color were noticed in the recipes with emulsion. The volume of the cookies before and after baking was significantly bigger for the cookie formulations with emulsion, which also affected the texture. The greatest crunchiness and firmness were noticed in the cookies with 100% replacement of the butter.

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Keywords: Healthy food, fat replacers, emulsion, inulin.

APPLICATION OF CHITOSAN EDIBLE FILMS FOR SHELF LIVE EXTENSION OF RAW TOMATOES

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Recently, edible films and coatings have been increasingly used in industry due to their characteristics and biodegradable nature. They are biodegradable, not harmful to the environment, play an important role in the reduction of environmental pollution, and are obtained from natural materials. As a result, this contributes to the increased use of edible films and coatings compared to synthetic films. Much attention has been paid to biodegradable polymers based on renewable sources, due to their wide range of application in the packaging process, agriculture and in the field of medicine.

In this research, chitosan - the second most abundant polysaccharide on nature after cellulose, was used as a biodegradable polymer. It forms clean, solid and flexible films with a good oxygen barrier, which may be employed as packaging, particularly as edible films and coatings, enhancing shelf life of a diversity of food products. Moreover, chitosan has several advantages over other biomaterials owing to its antimicrobial activity against a wide range of microorganisms. Modification of chitosan edible films were made by addition of aqueous garlic extract. The antimicrobial activity of aqueous garlic extract against mold isolated from rotten tomato was determined by the method of disk diffusion.

The aim of this study was to extend the shelf life of tomatoes by applying a chitosan edible film enriched with aqueous garlic extract.

Keywords: edible film, chitosan, aqueous garlic extract, antimicrobial activity, shelf life

IMPACT OF DIFFERENT VINIFICATION METHODS ON THE POLYPHENOLIC CONTENT IN RED WINES

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Polyphenols are large family of naturally occurring, structurally diverse, organic compounds abundant in plants. Phenolic compounds such as anthocyanins, flavonoids and tannins are important constituents of red wine contributing to the taste, color, mouthfeel and quality. They are also associated with the health-promoting properties of red wine. The proportion of the different polyphenols in wine depends on grape variety, maturity, temperature of maceration and fermentation and of the type of vinification. In this study, total phenols (TP), total anthocyanins (TA) and colour parameters of *VitisVinifera*red wines Vranec and Pinot Noir from vintage 2020, produced in the Republic of N. Macedonia, have been evaluated. Wines from both varieties have been produced with two winemaking techniques, including classical fermentation and roto process in order to study and compare the effect of vinification. Total phenols were determined using the Folin-Ciocalteu method at 765nm and expressed as gallic acid equivalent (GAE, mg/l) [1]. Determination of the total anthocyanins was realized by the method proposed by Di Stefano et al. [2]. The samples were diluted with a solution consisting of 70/30/1 (*v/v/v*) ethanol/water/HCl (concentrated) and the absorbance was measured at 540 nm. Colour parameters, including color intensity (CI) and hue (H) were determined by direct measurement of the wine absorbance at 420 nm, 520 nm and 620 nm. It was found that variety has an influence of the phenolic content, observing higher content of TP and TA in Vranec wines (TP: 1690 mg/l, TA: 248 mg/l) in comparison to Pinot Noir (TP: 1120 mg/l, TA: 236 mg/l) regardless the vinification method. Considering the influence of winemaking method, it was observed that the roto process gives better results and higher content of total phenols and anthocyanins, observed in both varieties.

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Keywords: Total phenols, anthocyanins, winemaking, red wine, spectrophotometry.

RHEOLOGICAL PROPERTIES OF FUNCTIONAL BISCUITS MADE WITH INCORPORATION OF GRAPE SKINS AND SEEDS FROM VARIETY "VRANEC"

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In this research the rheological properties of biscuits incorporated with grape skins and seeds (variety "Vranec"), a valuable by-product from grape juice industry were analyzed. Our purpose was to create functional biscuits that will have added nutritional value, furthermore to utilize food waste from one industry to another in the fashion of circular economy. 12 new biscuit formulations were produced with three different grape skins and seeds granulations (1, 0.5 and 0.25 mm) and their incorporation in the biscuits as partial replacement for the biscuit wheat flour in four different percentages (2.5, 5.0, 7.5 and 10.0%), compared to the reference made with 100% wheat flour. Four different methods for texture characterization using texture analyzer were performed: biscuit dough penetration, baked biscuits penetration, bolus method and saliva absorption. The goal was to determine the impact of the incorporated grape skins and seeds on the viscosity and the hardness of the biscuit dough before baking, the hardness and brittleness of the baked biscuit and its effects during chewing. The incorporation of the grape skins and seeds made the dough harder compared to the one without the seeds and skins. The hardness and the brittleness of the baked biscuits was also increased with the gradual addition of skins and seeds, and the most hard and brittle were the biscuits in which the smallest granulation (0,25mm) of powder was used. The bolus method showed that the hardness, stickiness, springiness, cohesiveness, chewiness and gumminess of the bolus made after mastication is greater for the referent biscuit formulation than the formulations made with grape skins and seeds in any granulation or concentration. The data analysis from the saliva absorption method showed that the addition of skins and seeds from grapes in the biscuits significantly shortens the chewing time and the number of bites needed to chew the whole biscuit before swallowing.

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Keywords: functional biscuits, grape skins and seeds, food waste, rheological properties

A SIMPLE HPLC-UV-DAD METHOD FOR DETERMINATION OF ACRYLAMIDE IN FOOD PRODUCTS

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Acrylamide is a known carcinogen that has been found in starch-based foods products obtained with heat-treatments [1]. Acrylamide formation and degradation in foods depends on presence of acrylamide precursors such as free amino acids (mainly asparagine), reducing sugars and processing conditions (i.e. baking time and temperature, moisture content of the product etc.) [2]. According to the European Food Safety Authority, coffee beans, potato chips and french fries have the highest levels of acrylamide. The aim of this study was to develop and apply a simple HPLC-UV DAD method for determination of acrylamide in potato chips, biscuits, crackers, bread and similar products. In order to extract the amounts of acrylamide from the tested food products, an ultrasound-assisted liquid extraction with acetone was used with prior defatting with hexane. The acetone extracted was evaporated to dryness and dissolved in water and the final extract was analyzed by reversed-phase HPLC coupled with diode array detection. The chromatographic analysis was performed with a Phenomenex Luna C18 column (250 × 4.6 mm, 5 μm) with gradient elution with mobile phase composed from acetonitrile and water. The retention time for acrylamide was 9,5 min with good linear response in the low UV range monitored at 200 and 222 nm. The obtained sensitivity was satisfactory enabling measurement of acrylamide present in quantities lower than 50 μg/kg. The method was used for analysis of products found on the market and was shown as a simple, fast, low-cost and robust alternative for the commonly proposed HPLC methods using tandem MS/MS detection for quantification of acrylamide.

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Keywords: acrylamide, HPLC-UV DAD, potato chips, biscuits, crackers, bread, acetonitrile

USING THE ESCAPE ROOM AND THE NEARPOD AS A NEW INNOVATIVE APPROACH IN CHEMISTRY TEACHING

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The rapid progress of the 21st century leads slowly to replacing the traditional teaching by the novel and contemporary teaching. It is known that chemistry is often considered as difficult subject that deals with abstract concepts, so the introduction of the new, creative, and innovative teaching methods would lead to overcoming this 'problem'.

In order to motivate the ninth-grade students, as well as to enable their active involvement in the class, the *Escape Room* and the *Nearpod* tool activities were applied during realization of the Exothermic and endothermic reactions topic. A novelty in contemporary teaching is the *Escape Room* activity [1], used as an educational game-based activity in teaching promoting creative thinking, teamwork, competitive spirit and interaction with students [2]. *Nearpod* is a digital platform for interactive distance learning that offers open-ended questions, quizzes, matching pairs activities, interactive virtual labs, and it can be used for synchronous or asynchronous activities. The opportunity of monitoring students' work during the class makes this tool very useful for formative assessment.

The sample comprised 244 ninth-grade students from five different primary schools in the Republic of Macedonia. Taking into accountthe fact that 2020/2021 school year the teaching was realized remotely, the lessons were conducted using MS Teams. The research was aimed at ensuring more active participation in the classes and increasing the interest and motivation of the students during the chemistry classes.Therefore, two questionnaires widely used in educational studies were adoptedas suitable instruments: Students' Motivation towards Science Learning (SMTSL) [3] and Intrinsic Motivation Inventory (IMI) [4]. The modified SMTSL questionnaire was used to examine the level of students' motivation to study chemistry, while the IMI questionnaire was used to assess students' opinions and experiences regarding the activities conducted in the class. The means, standard deviations and Cronbach's alpha were calculated using the software package SPSS Statistics 26. The analysis showed that this game-based approach contributes to students developing positive attitudes towards chemistry, increasing interest in the subject and gaining new knowledge.

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Keywords: chemistry teaching, Escape Room, exothermic and endothermic reactions, motivation, Nearpod.

INDUCED B-PHASE FORMATION IN POLY (VINYLIDENE FLUORIDE) COMPOSITE MEMBRANES USING TIPS METHOD

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Poly (vinylidene fluoride) (PVDF) is a semi-crystalline polymer which belongs to the class of ferroelectric polymers. It has unique electroactive responses including ferro-, pyro- and piezoelectric effects and high dielectric constant, making it an appealing material for energy generation and energy storage applications. PVDF can crystallize in five different phases referred as α, β, γ, δ and ε, among which the β-phase shows the best properties due to its all-trans planar zigzag conformation causing a large dipole moment and spontaneous polarization [1]. Based on previous researches the α-phase is kinetically favored and can be obtained by direct crystallization from the melt, while the β-phase is thermodynamically favored and its formation depends on the control of the processing parameters [2]. Most common approaches for obtaining high β-phase content in PVDF is by mechanically stretching, using external electric field, ultra-fast cooling and addition of nucleating fillers [3]. In this research we report formation of β-phase in PVDF/$BaTiO_3$ composites using thermally induced phase separation (TIPS) method. TIPS method relies on change in the temperature to induce de-blending of homogenous polymer solution which results in a multi-phase system. Composites with 5, 10, 15 and 20 wt. % $BaTiO_3$ particles were prepared through solution mixing, cast on clean glass and solidified, followed by immersion in non-solvent bath, resulting in porous composite membranes. For determining the β-phase content Fourier transform infrared spectroscopy (FTIR-ATR) was used. Scanning electron microscopy (SEM) was used for observing the membrane structure and dispersion of particles. Thermal analysis of the composites was performed using Thermogravimetric analysis (TGA). Crystallinity was calculated from X-ray diffraction (XRD) analysis. Results showed that the β-phase content increased with the addition of ceramic particles, reaching highest value of 73.8% for the composite with 20 wt. % $BaTiO_3$. The addition of ceramic particles also increased the crystallinity and lowered the degradation temperature of PVDF.

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Keywords: β-phase poly (vinylidene fluoride), piezoelectricity, phase separation, membranes, $BaTiO_3$

SYNTHESIS AND STRUCTURE-VIBRATIONAL ANALYSIS OF PEROVSKITES CONTAINING PbI6-OCTAHEDRA

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The constant need for more efficient alternative energy sources, such as solar energy, have contributed to a rapid growth in the interest towards perovskites, especially the hybrid organic-inorganic perovskites (HOIPs), which as efficient light absorbers, have had a great effect on enhancing solar cells functionality [1]. In this work, several perovskites with a general formula $APbI_3$ were synthesized including organic (methylammonium - MA^+, formamidinium - FA^+, guanidinium - GU^+, pyrrolidinium - PY^+ and dimethylammonium - DMA^+) or inorganic (Cs^+ and Rb^+) cations. The perovskites were chosen by prior exploration of their structural characteristics, in order to include perovskites with different dimensionalities, space groups and PbI_6 octahedra bonding and orientation [2, 3]. The synthesis of the perovskites was performed by solvothermal processes with variation in solvents and temperature in order to establish the optimal conditions. The synthesized samples were analyzed using powder XRD, infrared and Raman spectroscopy, both for their identification and structural characterization.

Detailed characterization of HOIPs by XRD is hard and misleading in some cases, due to subtle crystallographic characteristics of investigated compounds. In this work, Raman spectroscopy is suggested as a technique complementary to XRD that may be used to characterize organic-inorganic perovskites. The difference in hydrogen bonding, shape of the cation, distortion and position of the octahedra in perovskite structures influence the Raman spectra (shape, intensity and position of the bands), something that can be used for structure identification [4].

In this work, a detailed characterization of bands in the Raman spectra for each synthesized perovskite is performed, since for some of the compounds, there are no such data available in literature. This information is used to correlate the Raman bands with the specific structure and connectivity of octahedra. The correlations are made based on the frequency region of cage vibrations of PbI_6 octahedra, 10 – 200 cm^{-1}. Different types of octahedra connectivity results in differences in the position and intensity of the bands. In the future this information may be used for structural identification of other HOIPs and inorganic perovskites by Raman spectroscopy.

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Keywords: perovskites, photovoltaics, Raman spectroscopy, X-ray diffraction

INFLUENCE OF THE RARE-EARTH CATION SUBSTITUTION INRe$_{1-x}$Er$_x$FeO$_3$(Re = Sm or Gd, x = 0, 0.2 and 0.4)PEROVSKITES CHARACTERIZEDBY POWDER XRD AND VIBRATIONALSPECTROSCOPY

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Perovskites are scientific hotspot, extensively studied because of their versatility and flexible structure. The never-ending possibilities of partial substitutions at cationic positions result with complex perovskites having intriguing properties. Incorporating rare-earths into the structure of double perovskites opens up great possibilities for unique properties, which in the future may lead to brand new applications [1, 2].

Considering the above-mentioned, the main purpose of this research was to synthesize complex perovskites that contain rare-earths into their structure. Thereby, we had successfully obtained two perovskite series with general formula: $Gd_{1-x}Er_xFeO_3$ and $Sm_{1-x}Er_xFeO_3$ (x=0, 0.2 and 0.4). These compounds were synthesized by using the sol-gel method with citric acid as fuel. All procedures were done under controlled temperature and pH. For the analysis and identification of the obtained materials, X-ray powder diffraction, IR and Raman spectroscopy were used. The XRD patterns confirmed the purity of the synthesized products and revealed that they crystallize in the orthorhombic system. The unit cell parameters of the obtained perovskites were also determined. Infrared and Raman spectroscopy were used to characterize the obtained powders and also to confirm the partial substitutions of gadolinium/samarium with erbium. Based on the band shift observed in the Raman spectra that is a result of the substitution, one can judge about the influence of the cation that is incorporated in the structure. The region below 200 cm^{-1} in the Raman spectra carries valuable information about the distortion of the FeO_6 octahedra when another cation is inserted in the structure.

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Keywords: complex perovskites, rare-earths, sol-gel method, X-ray powder diffraction, IR and Raman spectroscopy

IMPLEMENTATION OF METHODS FOR DETERMINING AND MONITORING PERSISTENT ORGANIC POLLUTANTS IN AIR

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Persistent organic pollutants (POPs) are organic compounds of natural or anthropogenic origin that resist chemical, photolytic, or biological degradation [1]. They have low water solubility and high lipid solubility, which gives them high potential for biomagnification and bioaccumulation in fatty tissues of living organisms. POPs are semi-volatile chemicals (boiling points between 240 and 400 °C) of global concern owing to their ability for long-range transport via the atmosphere, away from their original sources. Due to concerns about their harmful effects to ecosystems and human health, the majority of POPs are banned or restricted around the world but even long-banned POPs can be still found in the environment [2]. Among the POPs, organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are considered as pollutants of special concern. This especially counts for regions with a history of production of lindane since its production has been accompanied by huge amounts of its byproducts and tons of hexachlorocyclohexane isomers (HCHs) have been deposited in dumpsites at more than 30 locations around the world [3].

In order to find a solution for this problem it is necessary to identify the air pollutants and estimate their concentrations. The goal of this research was to implement methods suitable for analysis of persistent organic compounds in air that will enable data collection about their presence and concentration levels. In this research, a method has been implemented for collection of semivolatile organic compounds from air using low-volume polyurethane foam (PUF) sampler and their subsequent desorption by Soxhlet extraction with 5% diethyl ether in hexane. The extracts were concentrated and analyzed using gas chromatography coupled with an electron capture detector.

Organochlorine pesticides and polychlorinated biphenyls in air were analyzed at three locations around the landfills at the former OHIS (Organic Chemical Industry Skopje) factory with high former production of OCPs. 12 different organochlorine pesticides and polychlorinated biphenyls were detected and quantified in the samples including α-HCH, β-HCH, γ-HCH, δ-HCH, hexachlorobenzene, heptachlor, aldrin, *o*,*p*'-DDD, endrin, PCB 101, PCB 118, PCB 153.

This research brought useful data about the concentrations of OCPs and PCBs at the investigated locations. The established methods can be further used for monitoring of OCPs and PCBs concentrations and seasonal variations. This will be the first study of its kind in our country and will also encourage regular monitoring of volatile organic compounds in air. Studying air pollution by these compounds is an important starting point for creating a sustainable monitoring program and improving air quality.

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Keywords: Persistent organic pollutants, organochlorine pesticides, polychlorinated biphenyls, low-volume PUF sampler, gas chromatography-electron capture detection

DYE-SENSITIZED SOLAR CELLS

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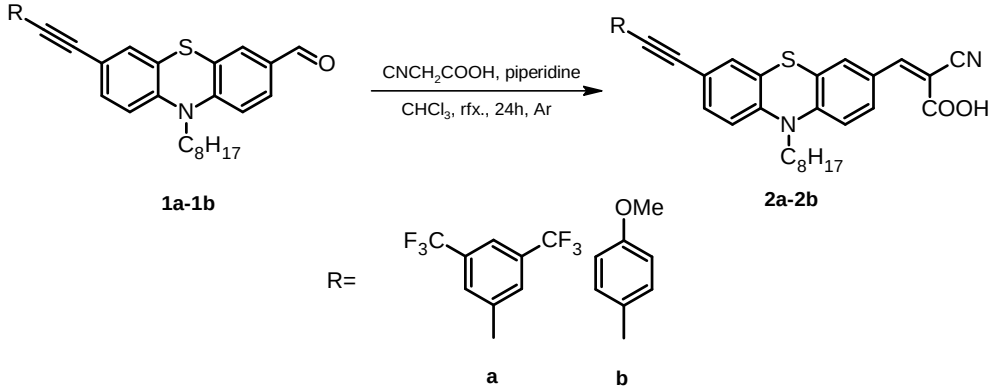
In recent years donor-acceptor (D-A) architecture compounds have found wide application in organic electronic devices, including active layers in dye-sensitized solar cells. System enrichment with additional electron-donating and withdrawing groups significantly improves the optical and thermal properties of the molecules. Due to the electron-rich sulphur and nitrogen heteroatoms, the phenothiazine ring is frequently used as a donor building block. Furthermore, an additional advantage of phenothiazine is the high possibility of structure modification, which allows to obtain extended D-A systems [1,2].



Scheme 1. The synthetic route for the preparation of compounds 2a–2b.

Two novel D/A–π–D–π–A dyes 2a and 2b were designed and prepared via a multi-step synthesis. Firstly, the phenothiazine ring was functionalized by alkylation, formylation, bromination and Sonogashira coupling reactions. In the final stage (Scheme 1) 10-octyl-10H-phenothiazin-3-carbaldehyde connected via acetylene linker with additional electro-donating (1a) or withdrawing substituent (1b) condensed with cyanoacetic acid as an anchoring group. Compounds 2a and 2b were characterized by NMR spectroscopy and elemental analyses. The impact of 3,5-bis(trifluoromethyl)phenyl acting as acceptor (A) and p-methoxyphenyl acting as donor(D) on the thermal and photophysical properties has been studied. The obtained results suggest that derivatives 2a and 2b can be used as a photosensitizer in DSSC devices.

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Keywords: phenothiazine, multi-step synthesis, donor-acceptor system.

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