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ANALĪTISKĀS UN FIZIKĀLĀS ĶĪMIJAS SEKCIJA

CONDUCTING POLYMERS BASED SENSORS AND BIOSENSORS BIOCOMPOSITE

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During this presentation, the most important research directions at NanoTechnas – Centre of Nanotechnology and Materials Science will be overviewed and discussed. The most important methods of conducting polymer synthesis will be introduced. Authors have invented and improved some new and/or advanced electrochemical [1], chemical [2] and biochemical [3–6] formation methods suitable for the formation of conducting polymer based layers. The applicability of conducting polymer based functional layers in the design of various types of electrochemical biosensors will be also discussed [6]. During this presentation significant attention will be focused on the development of glucose biosensors, mainly based on conducting polymer layers. Advantages and disadvantages in the application of glucose oxidizing enzyme – glucose oxidase (GOx) – will be discussed. During the enzymatic reaction the GOx is forming hydrogen peroxide, which is able to initiate the polymerization of some conducting polymers. In some our researches it was shown that this method is well suitable for the synthesis of conducting polymers: polypyrrole [3], polyaniline [4], polythiophene [5]. It was demonstrated that both dissolved and immobilized enzymes could be successfully applied in the enzymatic synthesis of conducting polymer-based nanoparticles and other structures. Enzymatic synthesis of nanostructures based on conducting polymers can be assigned to so called ‘green synthesis’ because except the monomer, which is required for the formation of conducting polymer any other environmentally harmful materials are applied in above mentioned enzymatic polymerization process. We also have demonstrated that formed nanostructures and nanoparticles shows good biocompatibility with living cells and when they were injected in living mice peritoneum. We have demonstrated that during such kind of synthesis of nanoparticles and/or nanostructured layers the enzymes becomes entrapped within conducting polymer layer. In some other our researches it was shown that redox processes that are part of metabolism of living cells can be applied for the synthesis of conducting polymer – polypyrrole (Ppy), and formed Ppy nanoparticles could be entrapped within cell wall of yeast cells. Therefore, such nanoparticles and nanostructured layers are suitable for the design of amperometric glucose biosensors, biofuel cells and some other bio-devices.

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TOMATO DRYING DYNAMICS STUDY FOR INCREASED ENERGY EFFICIENCY IN AGRICULTURAL PRODUCTION

ENERĢIJAS EFEKTIVITĀTE LAUKSAIMNIECĪBAS PRODUKTU ŽĀVĒŠANĀ

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This research tests potential of heat pumps as an energy efficient and environmentally friendly process for tomato, drying. Heat pump could also be utilized as a cooling mechanism for greenhouses in the hot season to further enhance its overall energy efficiency and usability in drying biomass. A multitude of tomato drying methods are described in literature, most of which are relying on some method or combination of methods of generating a flow of heated air over the product to dry it [1].

Various studies that tested air temperatures ranging from as low as 42 °C to as high as 90 °C have been reported. It is generally agreed that lower temperatures result in the highest quality of the product, while the higher temperatures significantly decrease the drying time. It can be summarised from the literature studies that 60 °C is an acceptable equilibrium between loss of product quality (i.e. taste, smell, colour and texture) and the time required for the process where higher quality and price products tends to choose lower temperature. [2]

Tomato drying dynamics were studied for temperature range 40 °C to 65 °C to match air to air heat pumps exhaust hot air temperature. The study was performed with a conventional household fruit-dryer with forced air circulation. Tomato samples grown in the research partner SIA Rītausma greenhouse were used. Air circulation and moisture were not measured. The drying dynamics was studied for Admiro and Roma tomato varieties at different ripeness stages and with different fruit sizes. The study also tested the effect of the slice size – 1/6 and 1/8 of the tomato. Drying time was defined as time needed to reach 90% loss of mass of the raw tomato.

In the study it was found that tomatoes can be dried successfully without spoilage even at temperatures as low as 40 C. Increase of the temperature from 40 °C to 60 °C decreased the drying time by 50% from 20 h at 40 °C to 10 h at 60 °C. Further drying time reduction was achieved by selecting elongated varieties of tomato and thinner slicing. No significant effect of the ripeness was observed. Hot air temperature from household type air-air heat pump was found to be sufficient for effective tomato drying industrial process.

This project is supported by EAFRD – The European agricultural fund for rural development, project Nr. 17-00-A01620-000013.

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IMPACT OF EXTRACTION METHODS ON TOTAL PHENOLICS AND FLAVONOIDS IN CHOKEBERRIES (*ARONIA MELANOCARPA*)

EKSTRAKCIJAS METOŽU IETEKME UZ KOPĒJO FENOLU UN FLAVONOĪDU SATURU ARONIJU (*ARONIA MELANOCARPA*) OGĀS

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In recent years, there has been growing interest in sources of bioactive compounds. Berries are known as plant material rich in phenolics, flavonoids, antioxidants and others biologically active substances. The isolation of bioactive compounds from chokeberry (*Aronia melanocarpa*) may improve human health [1].

In the research berries from five different geographic regions of Latvia were analysed. All collected samples were splitted in two parts, such that one part of them were frozen and second part were dried. In the result were prepared extracts from frozen or dried berries in 70% ethanol/water or 10% glycerine/ethanol mixtures. Extracts were prepared by maceration lasting three weeks and ultrasound-assisted extraction.

The analyses were carried out with UV/VIS spectroscopy. For obtained extracts were determined total phenolic content by Folin-Ciocalteu method and total flavonoid content.

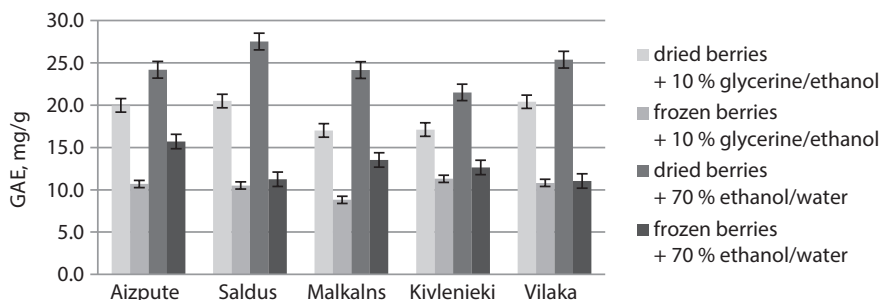


Figure. Total phenolic content (GAE) in chokeberries after 3 weeks maceration.

The preliminary results show that chokeberries have different phytochemical content that depends on type of storage (dried or frozen), extrahent (70% ethanol/water or 10% glycerine/ethanol mixture) and extraction method (maceration or ultrasound assisted extraction). Higher content of bioactive compounds is in chokeberries which extracts were prepared by using dried berries and 70% ethanol/water mixture. Results shows that ultrasound assisted extraction are more effective than maceration.

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SOME ASPECTS OF CONDUCTIVITY MEASUREMENTS BY IMPEDANCE ANALYSIS OF SULFONATED POLY(ETHER ETHER KETONE) MEMBRANES

DAŽI VADĪTSPĒJAS MĒRĪJUMU AR IMPEDANCES METODI ASPEKTI SULFONĒTA POLI(ĒTER ĒTER KETONA) MEMBRĀNĀM

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The proton transfer in hydrogen fuel cells is being carried out through polymer electrolyte membrane. Also, the CO₂ converters are using similar approaches as they can be considered as reverse fuel cells [1]. Proton conductivity of a membrane is one of the most important parameters as it is related to the fuel cell efficiency. Therefore, it is important to study and evaluate methods of conductivity measurements especially paying attention to exclude the parasitic contact resistance.

In this research we compare two methods of measuring proton conductivity of sulfonated poly(ether ether ketone) membranes using impedance analysis with different cell configurations [2]. The two methods are differential and single membrane method (Figure). Conductivity measurements were performed using Autolab potentiostat (from 50 kHz to 100 Hz, amplitude 10 mV) at RH = 100% and 295 K using Nafion membranes as reference.

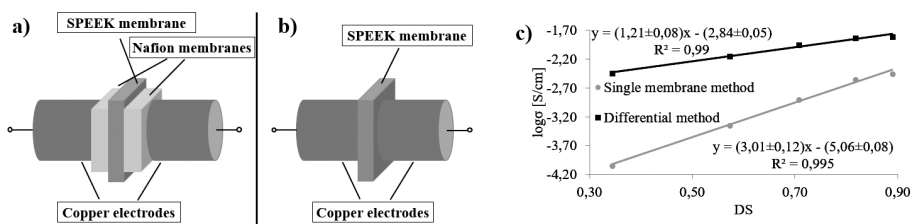


Figure 1. Different approaches to conductivity measurements: a) differential method, b) single membrane method and c) membrane conductivity as obtained by two approaches.

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ELECTROCHEMICAL STUDY OF PHOSPHOLIPID BILAYER FORMATION ON MIXED SILANE SELF-ASSEMBLED MONOLAYER ON OXIDE SURFACE

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The smallest living unit is considered to be a cell. Over couple of billion years of existing cells have developed means of protecting itself. The main organelle that is responsible for this is plasma membrane. It surrounds the living cell and consists of bilayer of phospholipids, cholesterol, oligosaccharides, integral and peripheral proteins. Membrane also controls what materials comes in and out of cell. So it has a few but important functions: protection and material transport. To investigate it more thoroughly, scientist began to immobilize bilayer membrane on solid surface. This would let them examine functionality of different membrane bound proteins.

One of the simple methods for phospholipid membrane immobilization is vesicles fusion. In order to achieve a relatively stable bilayer, first hydrophobic self-assembled monolayer (SAM) is deposited. For this work it was chosen octadecyltrichlorosilane (OTS) and methyltrichlorosilane (MTS) for mixed monolayer formation on fluorine doped tin oxide (FTO); 1,2-Dioleoyl-sn-glycero-3-phosphocholine (DOPC) and cholesterol at molar ration 6:4 for bilayer membrane formation (BLM). For characterization was chosen contact angle method (CA) cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

After SAM formation on hydrophilic FTO, the surface becomes hydrophobic, CA reaches 120°, which attests for organic layer formation. CV recorded in ferri-ferro solution using FTO electrode could be distinguished with typical redox peaks. But after SAM and BLM formation those peaks decreases and are no longer visible. EIS measurements reveals Cole–Cole spectra semicircular shape shrinkage after SAM and BLM formation, what is typical for bilayer membrane formation [1].

To sum up, phospholipid bilayer membrane formation on fluorine doped tin oxide was achieved. This BLM could be used for protein immobilization for future application.

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DEGRADATION KINETICS OF BIOMASS-BASED LEVO-GLUCOSENONE AND ITS INFLUENCING FACTORS

NO BIOMASAS IZDALĪTA LEVOGLIKOZENONA DEGRADĀCIJAS KINĒTIKA UN TĀS IETEKMĒJOŠIE FAKTORI

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Biomass is a valuable renewable resource, which can be used to produce not only heat and energy, but also materials and chemicals. Levoglucosenone (LGO) is best obtained by the depolymerization and dehydration of cellulose in the process of catalytic pyrolysis at comparatively low temperatures. [1].

In pyrolysis products LGO is most often determined by gas chromatography with flame ionization detector or mass spectrometry, but high-performance liquid chromatography (HPLC) has also been described in literature [2]. For the determination of LGO reversed phase HPLC is usually used with aqueous mobile phases, so the aim of this work is to evaluate the stability of LGO in aqueous solutions. Knowledge about the degradation trends of LGO in aqueous solutions is important for storage, sample preparation and analysis of pyrolysis products.

In this study LGO was determined by reversed phase UHPLC-UV with a mobile phase consisting of a mixture of water and acetonitrile, so the stability of LGO solutions in water and a water/acetonitrile (50:50) mixture was evaluated. The solutions of standard LGO, as well as a LGO containing sample of pyrolysis products were stored at 4 °C and 21 °C (± 1 °C) temperature for a month and analyzed with intervals of several days. Figure shows, how the concentration of LGO standard in the solutions decreased with time.

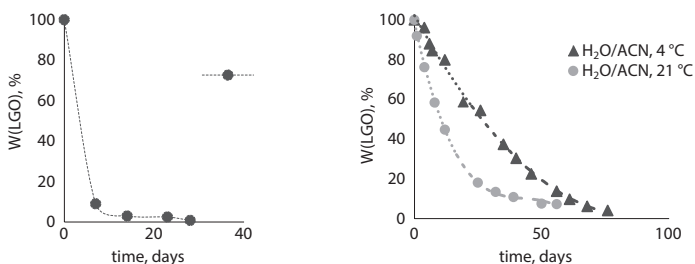


Figure 1. The decrease of the concentration of LGO in aqueous solutions at 4 °C and 21 °C

LGO degradation is the fastest in the aquatic environment. This is due to the effect of water as a polar proton donor solvent on the degradation rate. The acetonitrile additive slows the degradation rate of LGO. LGO degradation is influenced not only by the solvent but also by the storage temperature of the solution, at 21 °C, LGO degradation is faster.

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DEVELOPMENT OF TXRF METHOD FOR DETERMINATION OF CALCIUM AND PHOSPHORUS MOLAR RATIO IN HYDROXYAPATITES

TXRF METODES IZSTRĀDE KALCIJA UN FOSFORA MOLĀRĀS ATTIECĪBAS NOTEIKŠANAI HIDROKSILAPATĪTOS

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Hydroxyapatites (HAp) and other calcium phosphates, being similar to a chemical composition of human's bone inorganic fraction, nowadays are mostly recognized and widely used biomaterials for bone and teeth renewal. Performing quality control, Ca and P molar ratio (Ca/P) serves as an underlying analytical parameter indicating HAp properties and chemical composition. To measure Ca/P ratio quickly and precisely, a simple and low-cost analytical procedure is required.

Data gathered in the course of continuous investigation of different Ca/P determination methods showed that TXRF (Total Reflection X-ray Spectrometry) is the most applicable tool for this aim due to short analysis time, multi-element analysis ability and low hardware maintenance costs. Unlike classical WD/ED-XRF, TXRF is arranged in a special geometry – an incident beam impinges upon a sample below critical angle, making it much more sensitive technique. Until now TXRF method has been successfully applied to a great variety of different biological samples [1].

A key problem of TXRF is a small sensitivity of P analysis due to its relatively low $K\alpha$ line intensity. Other major drawback is difficulty in achieving uniform crystallization and distribution of sample containing elements putting analyzed solution on a quartz carrier and drying the droplet. Besides solving these problems, research also includes a suitable standard element for both element quantification and HAp solubility studies plus some validation basics to achieve higher accuracy.

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APPLICATION OF DERIVATIVE SPECTROSCOPY IN REAL SAMPLE ANALYSIS FOR MATRIX EFFECT REMOVAL

ATVASINĀJUMA SPEKTROSKOPIJAS IZMANTOŠANA MATRICAS EFEKTA NOVĒRŠANAI REĀLO PARAUGU ANALĪZĒS

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Caffeine is a key component of tea, which determines its favorable effect on human's health and high popularity of this beverage all over the world. Caffeine can be quantified by different methods (non-aqueous titrimetry, gravimetry, IR-spectroscopy, UPLC), though in analytical laboratories a preference is usually given to spectrophotometry due to its simplicity and availability.

As a basis for laboratory work development a photometric procedure described by Dobrinas *et al.* [1] was used involving interfering compound (such as tannins) precipitation in tea water extract and absorbance measurement of a filtrate at 273,5 nm wavelength. Since a studied manuscript has several imprecisions related to absorbance measurement technique and lacks information on occurring reaction mechanisms, method robustness and suitability for analysis of different sorts of tea, a more detailed research on these ambiguities is required.

To consummate quantification procedure, specialties of different tea sorts analysis were assessed, used reagent concentration (notably pH) influence on interfering agent precipitation degree was established, as well as spectra processing methods (derivative spectroscopy) to minimize matrix effects were studied. For more effective elaboration several physical techniques were embraced: XRD (to determine sediment composition), FT-IR (to follow extract composition changes during sedimentation) and LC-MS (to identify other tea components at respective wavelength).

Laboratory work "Quantitative caffeine determination in tea" will be introduced in a Master's programme course "Spectrometric analysis methods" starting from 2019 spring semester.

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REGIONAL MACROECONOMIC IMPACT OF NUCLEAR POWER PLANT CONSTRUCTION IN THE BALTIC STATES

ATOMELEKTROSTACIJAS BŪVĒŠANAS REĢIONĀLĀS MAKROEKONOMISKĀS IETEKMES NOVĒRTĒJUMS BALTIJAS VALSTĪS

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Macroeconomic impact (MI) of NPP construction on the Baltic States was studied using spreadsheet based model 'BRImpacts' created by the researchers of the Lithuanian Energy Institute and applied to the Baltic States for the first time.

The model is based on social accounting matrix (SAM) framework [1]. MI of nuclear projects at large extent depend on the factors that are not covered by traditional input-output tables and their capability to depict a broad range of properties of nuclear projects is very limited. The social accounting matrix depicts 19 activity and commodity groups, labour and capital as production resources, various transactions, households, corporations, government and the rest of the world sectors. Entire Baltic region – Estonia, Latvia and Lithuania was analyzed in two different modes: foreign and domestic-sourced investments. 2010 statistical data were used while industrial participation factors were estimated as a part of the work within BRILLIANT collaboration.

The analysis reveals that for the NPP construction period a positive impact on GDP is expected only in the case when investment is financed by foreign savings and does not affect the investment formation in other activities of the domestic economy. Employment impacts reflect the same trends as the GDP. The general trend is that more positive impacts are observed in regional cooperation cases. Quantitatively NPP financing by domestic investment has a significant negative impact on the GDP during the construction, while financing from external sources has a moderately positive effect on GDP.

The regional cooperation makes NPP construction more attractive. Increase in local participation levels is a good way to obtain more positive macroeconomic impacts of nuclear investments. The availability of foreign investment or another non-domestic financing source along with a fair risk allocation would be a crucial factor in the success of nuclear power in the Baltic region.

Acknowledgement: This work has received funding from the EURATOM research and training programme 2014–2018 under grant agreement no. 662167 (BRILLIANT project).

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DETERMINATION OF RESIDUES AND METABOLITES OF MORE THAN 140 PHARMACOLOGICALLY ACTIVE SUBSTANCES IN MEAT BY LIQUID CHROMATOGRAPHY COUPLED TO HIGH RESOLUTION ORBITRAP MASS SPECTROMETRY

VAIRĀK KĀ 140 FARMAKOLOĢISKI AKTĪVO VIELU UN TO METABOLĪTU NOTEIKŠANA GAĻĀ IZMANTOJOT ŠĶIDRUMU HROMATOGRĀFIJU – AUGSTAS IZŠĶIRTSPĒJAS MASSPEKTROMETRIJU

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This study reports an analytical method for simultaneous identification, screening and quantification of 164 residues and metabolites of pharmacologically active substances belonging to such therapeutic classes as anti-infectious (antibiotics and chemotherapeutics), anti-inflammatory and antiparasitic agents (against protozoa, endo- and ectoparasites), corticoids and agents acting on the nervous and reproductive systems, substances with hormonal and thyreostatic action, and beta agonists. Different sample preparation procedures were compared and optimised for the detection of selected veterinary drugs in chicken, porcine and bovine meat by ultra-high performance liquid chromatography coupled to high-resolution Orbitrap mass spectrometry.

The optimised instrumental method and sample preparation procedures were validated according to regulation 2002/657/EC [1] by fortifying blank matrix at four levels (0.5, 1.0, 1.5, and 2 times the maximum residue limit (MRL, defined in the Commission Regulation 37/2010/EC)), or at concentrations as low as possible for substances without an MRL. The evaluated performance parameters were selectivity, matrix effect, method and instrument limits of quantification, accuracy, and repeatability.

Finally, the method was successfully used to detect and quantify veterinary drug residues in real samples found to be suspect using the non-selective qualitative test for the detection of inhibitor substances. The results were confirmed using the relevant one-residue confirmatory methods revealing concentrations of residues higher than MRLs established for several samples.

Acknowledgement: This research was co-financed by ERDF (85%) and the state budget of Latvia (7.5%) under the project No. 1.1.1.1/16/A/258.

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EVALUATION OF SELECT BUFFERS FOR SIMULTANEOUS DETERMINATION OF IONIC AND ACIDIC PESTICIDES BY ION CHROMATOGRAPHY AND MASS SPECTROMETRY

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Suppressed ion chromatography with mass spectrometric detection requires complex equipment to eliminate the inorganic buffer before introduction of eluate into the ionization source [1]. Loss of analytes and peak broadening may also occur during suppression. A technique not requiring complex suppression equipment would be a straightforwardly applicable approach. Ammonium carbonate, oxalate and salicylate were tested and triethylammonium bicarbonate, citrate and edetate buffers were evaluated for simultaneous trace determination of ionic and acidic pesticides. 23 pesticides, different in physicochemical properties ($\log P < 0$, $\log P \geq 0$) and structure (carboxylate, phosphonate, azolide, azanide, phenolate, bromate and chlorate), were determined in solvent and spiked beer and oat extracts. Two ionization sources were compared with respect to application of non-volatile buffers. Design of ionization source was found critical for application of non-volatile buffers.

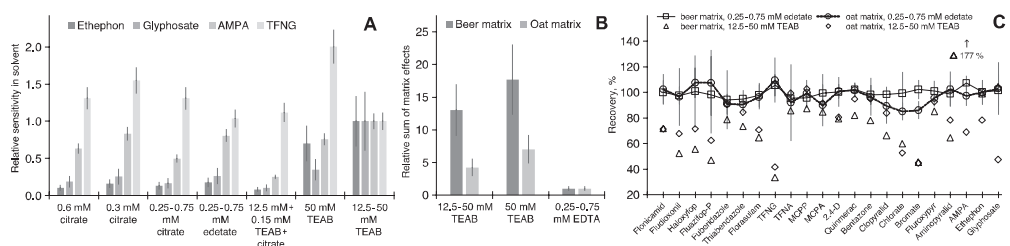


Figure. (A) – Relative sensitivity in solvent; (B) – relative sum of matrix effects for spiked beer and oat extracts; (C) – recoveries of analytes from spiked beer and oat extracts in case of different buffers.

Choice of buffer strongly influenced matrix effects. With triethylammonium bicarbonate gradient, where most pesticides eluted at 12.5 mM, sensitivity improved in standard solutions, but lead to exacerbated matrix effects in case of spiked extracts. Ionic and acidic pesticides were quantified in spiked beer and oat extracts with recoveries 80–110% using a QTrap[®] mass spectrometer with TurboV[™] electrospray ionization source after a gradient separation with edetate buffer on a Metrosep[®] A Supp 5 anion exchange column.

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BIOCOMPOSITE WITH POLYPYRROLE, CARBON NANOTUBES AND SACCHAROMYCES CEREVISIAE ELECTROCHEMICAL INVESTIGATION

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Nowadays science is pushing forward to develop environmentally friendly ways of producing energy. Microbial fuel (MFC) can generate an electrical current from the metabolic reactions which occur internally towards an external electrode. The power output differs depending on the conditions: microorganisms and their catalytic activity, biocompatibility, mediators used, electrode surface, immobilisation method. Much research is put forth to develop more efficient MFC current densities to put into practical use [1]. The main target is to improve the charge transfer from a microorganism towards an electrode.

In this study we are changing the cell's wall resistance into one with better conductivity by encapsulating the cell with polypyrrole [2] and carbon nanotubes [3]. Polypyrrole is an electrically conductive polymer, carbon nanotubes are highly conductive and both are biocompatible at certain concentrations. We are hoping of establishing a better electrical connectivity between the *Saccharomyces cerevisiae* cells and the electrode's surface. In our experiment, we are also using different mediators: a hydrophilic – potassium ferricyanide and a lipophilic 9,10-pheanthrenequinone for carrying out the electrical charge in a series of redox reactions. Varying cell modifications as biocomposites have a different impact on the generated electrical current. Cyclic voltammetry gives us insight on the intracellular metabolic processes of the cell and the extracellular redox processes. The biocomposite bioelectrochemical processes will be discussed in the conference poster and the potential for bioelectrochemical device applicability.

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INCORPORATION OF FLUORINATED AMINO ACIDS INTO ALZHEIMER'S A β 42 PEPTIDE FOR STUDIES OF ITS AGGREGATION MECHANISM

FLUORĒTU AMINOSKĀBJU INKORPORĒŠANA ALCHEIMERA A β 42 PEPTĪDĀ TĀ AGREGĀCIJAS MEHĀNISMU PĒTĪŠANAI

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Alzheimer's disease (AD) is a progressive neurodegenerative disease that affects many people worldwide. Amyloid-beta (A β) peptides play the main role in the progress of the disease. These peptides have a tendency to form aggregates in the central nervous system. The predominant isoform in the amyloid aggregates is the 42-residue peptide A β 42. Intensive studies have been performed to understand the detailed mechanism of A β aggregation. Unfortunately, there is little progress in these studies. NMR spectroscopy is an excellent method to decipher molecular mechanisms. However, NMR requires production of peptides with magnetically active nucleus labels. Fluorine is an attractive NMR label with high sensitivity (83% of that of the proton) and 100% natural abundance. The chemical shift of the ¹⁹F nucleus is extremely sensitive to the surrounding environment, so it can be used to monitor changes in protein conformation that mostly are not detectable using other techniques [1, 2].

Investigation of aggregation mechanisms requires the production of large amounts of pure A β peptides in monomeric form. In our study, we used a construct (NT*A β 42), in which the A β 42 peptide is fused with solubility enhancing tag derived from a spider silk protein [3]. We present a method for high yield protein expression in *E. coli* and purification of the fusion protein and its fluorinated analogue for obtaining the peptides in monomeric form by nickel affinity, desalting and size exclusion chromatography and lyophilisation. Obtained proteins and peptides were studied and characterized by MALDI-TOF mass spectrometry, UV-Vis spectroscopy, SDS-PAGE, and NMR using 2D [¹⁵N-¹H]-HSQC, ¹H, and ¹⁹F experiments.

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DETECTION OF C4 PLANT SUGAR IN ADULTERATED HONEY USING IRMS AND UHPLC

C4 AUGU IZCELMES CUKURU NOTEIKŠANA VILTOTĀ MEDŪ IZMANTOJOT IRMS UN UHPLC

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Honey can easily be adulterated with various cheaper sweeteners for higher commercial profits. Commonly used adulterants include high fructose corn syrup, maltose syrup, refined beet and cane sugar etc. Stable isotope ratio mass spectrometry (SIRMS) can be used to determine the adulteration of honey with C4 plant (corn or cane) sugar since its $\delta^{13}\text{C}$ values are around -10‰ to -20‰ but bees use floral nectar from C3 plants which $\delta^{13}\text{C}$ values are about -22‰ to -33‰ . Significant $\delta^{13}\text{C}$ value difference between honey and its protein provide valuable information of honey authenticity [1, 2].

Five adulterated honey samples were made adding different weight fraction of sugarcane sucrose syrup (3%, 6%, 9%, 12%, 15%). The protein from the honey was extracted using dialysis membrane with MWCO 12 kDa. Determination of $\delta^{13}\text{C}$ ratios in protein and honey was carried out with Nu Horizon SIRMS at the University of Latvia, using certified inorganic reference materials USGS-40 and USGS-41 (L-Glutamic acid). The $\delta^{13}\text{C}$ values are expressed relative to VPDB. Waters Acquity UPLC system with Waters Acquity UPLC BEH Amide column (100 mm \times 2,1 mm, \varnothing 1,7 μm) combined with Waters ELSD detector were used to determinate amount of sucrose content in pure and adulterated honeys.

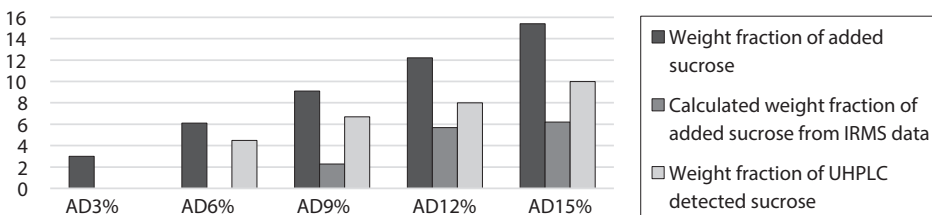


Figure. Weight fraction of sucrose in adulterated honey

Despite dissimilar results of calculated and detected weight fraction of sucrose to actually added weight fraction, results show expected increase in $\delta^{13}\text{C}$ values as C4 plant adulterant concentration increases to honey. Only adulterated honeys with added sucrose content higher than 6% weight fraction have high enough $\delta^{13}\text{C}$ value difference between honey and protein to calculate amount of added sucrose. UHPLC method did not provide exact quantitative information to components which weight fraction is lower than 5%.

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DETERMINATION OF BISPHENOL A IN WATER BODIES OF RIGA

BISFENOLA A SATURA NOTEIKŠANA RĪGAS ŪDENS TILPNĒS

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Bisphenol A (BPA) is an industrial chemical primarily used to make polycarbonate plastic and epoxy resins. BPA has become the most manufactured chemical compound in the world, reaching 3.7 million tonnes per year [1]. Many years BPA was considered neutral to human and animal health, but toxicological and biochemical studies showed that BPA has estrogenic properties and agonistic effect; activity has been found even at low concentrations. In a project commissioned by the European Commission the no observed effect concentrations for BPA in marine water and freshwater were estimated [2].

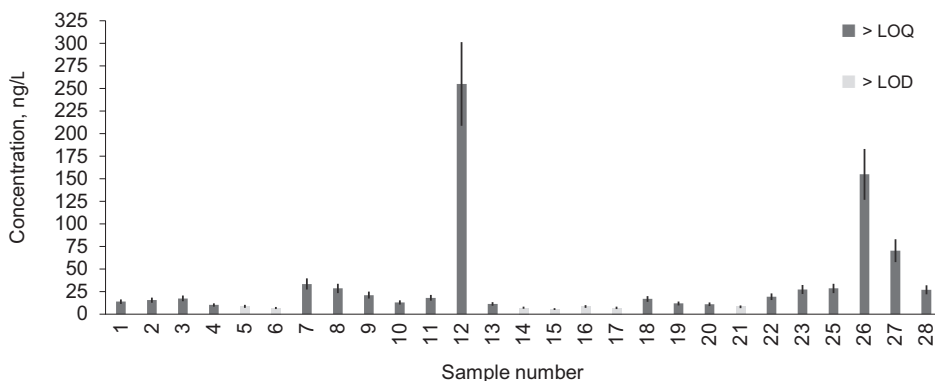


Figure. Concentration of bisphenol A in 28 samples from water bodies of Riga.

We analyzed surface water samples from water bodies of Riga in order to draw a first estimate of the level of pollution by BPA. An HPLC-MS/MS method for determination of BPA was used. Sample preparation consisted of filtering and solid phase extraction (SPE). Fast chromatographic separation on octadecyl bonded silica phase and tandem mass spectrometric detection was used to quantify BPA in 28 water samples from several districts of Riga. The concentration of BPA in surface water samples was from above the LOD of 4.1 ng L^{-1} up to 255 ng L^{-1} . Significantly higher concentration of BPA was determined in water samples located near areas of high industrial or commercial activity, such as near a market, railway or an automobile repair shop. The determined concentrations of BPA were below the proposed value of 1500 ng L^{-1} for freshwater in the report commissioned by the European Commission.

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C₆₀ MOLECULE SELF-ASSEMBLING IN A VOLUME OF EVAPORATING DROPLETS

C₆₀ MOLEKULU PAŠAPVIENOŠANĀS IZTVAICĒJOŠO PILIENU TILPUMĀ

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Currently, one of the most important fundamental questions of the modern nanoscience is development of relatively inexpensive highly efficient methods for the synthesis of new nanoscale structures and nanomaterials with new unique physico-chemical properties.

At the same time, there were new experimental data revealing that C₆₀ molecules have tendency to self-assembling and formation of large negatively charged (C₆₀)_m aggregates (where m is a number of fullerene molecules in aggregate) of different shapes and sizes in a wide range of mono- and multi-component organic solvents [1], as well as in the volume of evaporating droplets of organic solutions [2]. Aggregation of fullerene molecules may cause significant changes in their chemical and physical properties and result in a dramatic change in their medical, biological, technical and other applications.

In this work, the self-aggregation of fullerene C₆₀ molecules in the volume of evaporating droplets of fullerene xylene solutions on the flat surface of a glass at room temperature have been experimentally investigated for the first time. For C₆₀ molecule self-aggregation study process such methods as SEM and optical spectroscopy (FTIR, UV/VIS spectroscopy) were used.

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CHEMICAL CHARACTERIZATION OF SEVERAL HARDWOOD BARKS AS A RAW MATERIAL OF VALUABLE COMPOUNDS

LATVIJĀ AUGOŠU LAPU KOKU MIZU ĶĪMISKAIS RAKSTUROJUMS KĀ VĒRTĪGU SAVIENOJUMU IZEJVIELAI

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Nowadays the dependence of mankind on fossil energy resources, such as oil and its derivatives, is increasing. The use of these resources and their depletion cause various political and environmental problems. In order to reduce oil consumption and hence its environmental impact, more attention is now being paid to biorefinery concept [1]. Biorefination is defined as sustainable and synergistic biomass processing in marketable food and feed ingredients, products (chemicals, materials) and energy (fuel, electricity, heat) [2]. In Latvia, one of the potential sources of biomass is the timber industry, where a significant amount of tree bark is produced as production waste. To use bark material as a biomass feedstock, this bark material needs to be comprehensively characterized.

In this study barks of pine, aspen, grey alder and commercially grown plantation species of Salix, "Klara", were characterized. In order to evaluate the changes in the chemical composition of the pine bark depending on the location in stem, two samples were collected below 4 meters and above 4 meter. Chemical characterization of the bark includes extractive content, total lignin and cellulose content with accordance to industry (TAPPI) standards and comparison with results acquired from analytical pyrolysis. The most prominent compounds in barks were determined. Highest cellulose content was found in aspen bark (23.8±0,5 %) and pine bark (above 4 m) (24,1±0,8 %). Impossibly high total lignin content was found in pine bark (below 4 m) and grey alder bark with 46,8±0,7 and 40,7±0,3 % respectively. This can be explained with incomplete extract separation which can lead to increased results.

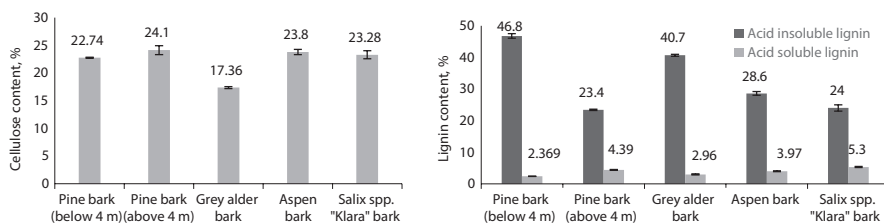


Figure 1. Total cellulose content (left) and lignin content (right) in wood bark samples

The determination of the most prominent compounds in the barks showed its potential use as a raw material for these compound obtaining.

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SOLID PROPELLANT STABILIZER DETERMINATION USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY TANDEM MASSPECTROMETRY (HPLC-MS)

CIETO PROPELANTU STABILIZATORU NOTEIKŠANA, IZMANTOJOT AUGSTI EFEKTĪVO ŠĶIDRUMA HROMATOGRĀFIJU TANDĒMĀ AR MASSPEKTROMETRIJU (AEŠH-MS)

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Solid propellants are high energy materials used in ammunition and rockets, usually consisting of nitrocellulose (NC), nitroglycerine (NG) and other additives, like mineral jelly, camphor and stabilizers. Although they are safe to handle and store for many years, NC degrades over time, producing various nitrogen oxides and acids in the matrices. This process is not only autocatalytic, but also exothermic, which can lead to autoignition of ammunition¹.

In order to stop this autocatalytic process, stabilizers like diphenylamine and centralites are added. These compounds stabilize propellants by scavenging nitrogen oxides and becoming stable nitro compounds. Therefore, the amount of stabilizers in propellants is the measure of safety and it must not drop below 0.2 % of the total mass². Also it is possible to estimate the amount of stabilizers left in future by subjecting propellants to forced aging with isothermal heating. To make the prediction more accurate, we need to determine activation energies of stabilizing reactions for each stabilizer in each kind of matrices³. To do so, we need a quick, cheap and reliable analytical method. We use very simple sample preparation method and ensure reliability by using massspectrometry. In further research this method will be used to determine stabilizer activation energies which will improve the kinetic model of propellant stabilizers.

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TRIBUTYL TIN DETERMINATION IN SURFACE WATERS USING GAS CHROMATOGRAPHY COUPLED TO INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

TRIBUTILALVAS NOTEIKŠANA VIRZEMES ŪDEŅOS IZMANTOJOT GĀZU HROMATOGRĀFIJU TANDĒMĀ AR INDUKTĪVI SAISTĪTĀS PLAZMAS MASSPEKTROMETRIJU

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Organic tin compounds, like tributyltin (TBT), is a major health and environmental hazard and, because of TBT's nonpolar butyl groups it is known to bioaccumulate in lipid tissue and liver [1]. Furthermore, TBT has been used as a biocide in anti-fouling paints for ships where its toxic effects were utilized to prevent sea organisms from growing on ship hulls and impeding sailing speed. Although TBT is banned globally it is still being reported in water samples around the world [2].

In order to distinguish organotin from inorganic tin compounds, TBT is first derivatized and then separated on GC, finally ultra-trace determination is possible due to inductively coupled plasma mass spectrometer detector which provides necessary sensitivity in ppt and even ppq level [3].

In this work several inland surface waters have been monitored for TBT and so far no positive samples have been discovered, this is mainly due to the fact that there shouldn't be any TBT in inland waters, like rivers, lakes, ponds etc. Nonetheless, we will continue to monitor TBT in surface waters in case an unexpected source of TBT suddenly appears and threatens environmental safety.

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CHARACTERIZATION OF C10-C17 CHLORINATED PARAFFINS IN OVEN-BAKED PASTRY PRODUCTS AND UNPROCESSED PASTRY DOUGH BY HPLC-Q-TOF-MS

C10-C17 HLORĒTO PARAFĪNU NOTEIKŠANA KONDITOREJAS IZSTRĀDĀJUMOS UN NEAPSTRĀDĀTĀ MĪKLĀ AR AEŠH-Q-TOF-MS

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Chlorinated paraffins (CPs) are increasingly recognized as a serious environmental concern [1]. In recent years, several studies on dietary exposure of CPs have emphasized that more attention must be paid on their prevalence in foodstuffs. Our study presents an HPLC-Q-TOF-MS based method for characterization of short-chain CPs (SCCPs, C₁₀₋₁₃) and medium-chain CPs (MCCPs, C₁₄₋₁₇) in oven-baked pastry products (N = 38) and unprocessed pastry dough material (N = 15).

Results revealed that ΣSCCP concentrations (expressed on dry weight) in product samples ranged from 0.3 to 23.0 ng/g (mean: 6.3 ng/g), while for dough from 5.8 to 22.8 ng/g (mean: 12.9 ng/g). Regardless of the sample matrix, the most abundant CP homologue groups were hepta- and octa- chlorinated undecanes and dodecanes. The average chlorination degree found in dough samples fell within a range of 55 to 60% (w/w). Meanwhile, a slight decrease of CP chlorination degree was observed for oven-baked products, in particular for C₁₀-C₁₂ SCCPs, thus displaying that a thermal decomposition of CPs occurs even in relatively mild conditions. Our findings imply that more attention must be paid to the presence of CPs in foodstuffs along with risks posed by their thermal degradation products.

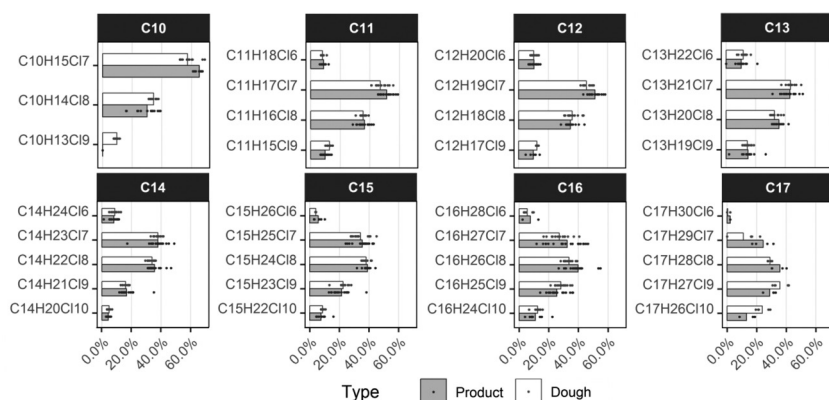


Figure. Profiles of CP homologues – relative distribution of SCCP and MCCP peak areas

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$\delta^{15}\text{N}$ AND $\delta^{13}\text{C}$ VALUES AS POSSIBLE MARKERS FOR DISTINGUISHING OF TYPE AND ORIGIN OF HUMIC SUBSTANCE

$\delta^{15}\text{N}$ UN $\delta^{13}\text{C}$ VĒRTĪBAS KĀ POTENCIĀLI MARKĪERI HUMUSVIELU VEIDA UN IZCELSMES ATŠKIRŠANAI

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Humic substance has a lot of different ways of use such as agriculture, brownfield environmental recultivation, medicine and pharmacy. It is important to know origin of humic substances which will be used for products that are used by people, to control possible pollution. Stable isotope ratio mass spectrometry (SIRMS) can be used for determination of origin of humic substance.

In the research humic acids samples from Latvia and other countries were analysed. The Latvian humic acids were isolated from peat samples that were obtained from Latvian State Forestry Institute Silava, manufactory humic substance samples were obtained from University of Latvia, Department of Environmental Studies.

The analyses were carried out with Nu Horizon SIRMS at the University of Latvia, using certified inorganic reference materials USGS-40 and USGS-41 (L-Glutamic acid). The $\delta^{13}\text{C}$ values are expressed relative to PDB and the $\delta^{15}\text{N}$ values relative to AIR.

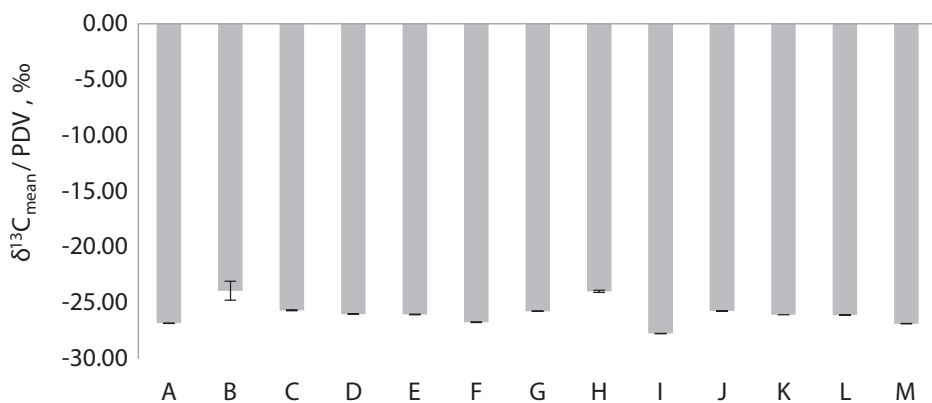


Figure. $\delta^{13}\text{C}$ values of manufactory humic substances.

The preliminary results show that the $\delta^{13}\text{C}$ values of some manufactory humic substances that are from one origin or same type have similar results. Manufactory humic substance can be used as reference material for humic acids that were isolated from Latvian peat.

ANALYSIS OF FINE AND COARSE PARTICULATE MATTER ORIGINATED FROM FIREWORKS

SMALKO UN RUPJO AEROSOLU DAĻIŅU ANALĪZE UGUŅOŠANAS LAIKĀ

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There are historical evidences that fireworks originally were developed already in the second century B.C. Starting from the 21st century, scientists are beginning to worry more about air pollution that occurs directly during the fireworks and in resent 5–7 years more and more studies are focused on the short term air quality degradation.

The use of fireworks creates an unusual and distinctive anthropogenic atmospheric pollution event, what may cause not only harmful health effects but seriously reduces visibility due to generation of dense, slowly disappearing clouds and affects the climate overall. [1] Therefor PM₁₀ and PM_{2.5} aerosols were sampled in Riga, during the firework episodes of the Independence Day celebration on November 18th, 2017 and 2018 and during New Year celebration firework. The other set of PM₁₀ and PM_{2.5} were collected during usual daily situation for background pollution control. The main purpose of the current research was to characterize chemical composition of coarse (PM₁₀) and fine (PM_{2.5}) particulate matter fractions by the ICP-MS.

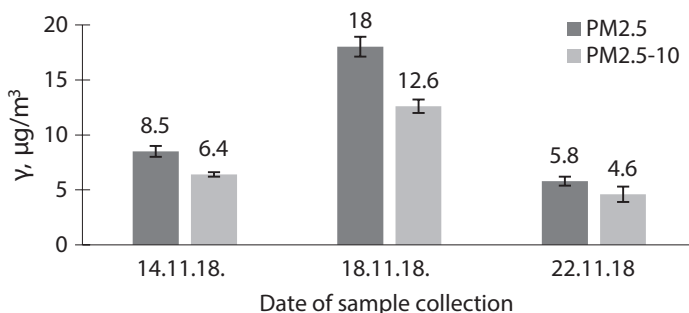


Figure. Aerosol particle mass concentrations during firework and daily data.

The analysis showed that in aerosols from the firework episode were detected: K, Ba, Sr, Cu, Al and Mg. Comparing results with daily data, metallic elements of aerosol particle fractions from fireworks, contain more than 2× till 19× higher concentrations. The analysis also showed that aerosol particle mass concentrations during firework is 3× higher than daily.

References:

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A SIMPLE HYDROTHERMAL METHOD FOR SYNTHESIS OF TITANIUM OXIDE WITH NEW PROPERTIES

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Titanium oxide is a well known material with wide range of applications such as solar cells, sensors, waste water treatment, etc. Titanium oxide application areas especially depends on phase and crystal structure composition, surface morphology, band gap. Due to this fact there is a high interest in synthesis of new titanium oxide structures with new properties in order to extend its application. Thus, there is a high demand of a simple and efficient method for the production of new materials with the desirable properties [1, 2].

This research is dedicated to show a simple hydrothermal method for the synthesis of controllable composition titanium suboxides from the aqueous solutions and to extend titanium oxide applications due to new properties, such as significantly lower band gap and nanoplatelet-shaped surface morphology. In order to prove the formation of titanium suboxides, EPR and XRD were employed. Ellipsometry was used to measure the thickness and band gaps of the films. It was determined that band gaps varies from 3,2 eV to 1,29 eV depending on the oxide composition. Calculations showed that porosity of titanium suboxide films are nearly 80%, what could be very important for application of these products in the gas sensing.

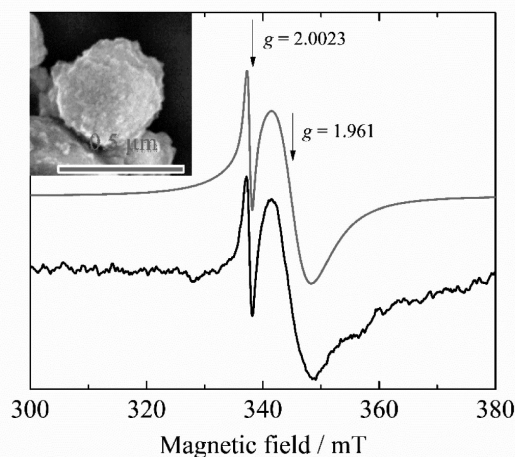


Figure. Experimental (black) and simulated (red) CW EPR spectrum of titanium particles.

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TGA/FT-IR AS A METHOD IN POLYURETHANE MATERIAL PYROLYTIC DESTRUCTION GASEOUS PRODUCT ANALYSIS

TGA/FT-IR KĀ METODEDE POLIURETĀNA MATERIĀLU PIROLĪTISKĀS DESTRUKCIJAS GĀZVEIDA PRODUKTU ANALĪZĒ

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Throughout the industry, most polymers are created using monomers derived from petroleum based feedstocks, the use of oil for energy and other uses coupled with the knowledge that as a source it is finite has led to research in renewable sources of monomers [1].

In this research rigid PU foam samples made from renewable material (tall oil) based polyols were analysed and compared to a rigid polyurethane (PU) foam material made from commercially available polyols. The evaluated properties of the materials were thermal degradation stability and the relative amount of gaseous waste products produced during the thermal degradation.

The analyses were done using Exstar SII TG/DTA 6300 thermogravimeter and Bruker Vertex 70V TGA/FT-IR spectrometer at the University of Latvia, within thermal range $T_{\text{room}}-T_{700}$ °C in N_2 gas flow. A part of the results of rigid PU foam analyses is shown in Figure.

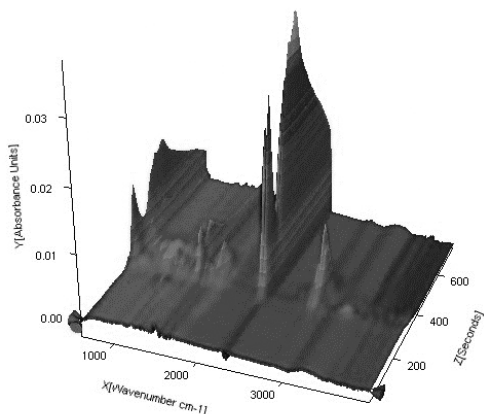


Figure. Rigid PU foam FTIR analysis

The preliminary results show that the presence of the renewable material based polyol improves the thermal degradation stability compared to the reference material used in construction. However, the FTIR results indicate an influx of gaseous waste products in both inorganic and organic form from all three experimental formulations during the thermal degradation processes, mostly in form of CO_2 , primary and secondary amines among other gaseous materials. Samples with lower renewable material content released a higher amount of gaseous waste products numerically.

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NON-TARGETED SCREENING AND IDENTIFICATION OF COMPOUNDS IN PAPER FOOD CONTACT MATERIALS

NEMĒRĶĒTS SKRĪNINGS UN SAVIENOJUMU IDENTIFICĒŠANA PAPIĀRA PĀRTIKAS KONTAKTMATERIĀLOS

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Following the recent vote of Members of European Parliament on upcoming proposal for a directive of the European Parliament and of the Council on the reduction of the impact of certain plastics products on the environment [1], there is an increased awareness regarding the replacement products of single use plastics. For single use plastics there are readily available solutions, however, there is no certainty about the overall benefit of the proposedly ecologically safer and compatible materials used for the manufacture of the replacement products.

The scope of our research is to evaluate of safety of paper straws as a replacement product. There are no guidelines present regarding the testing of paper food contact materials (FCM), hence, an approach used for FCM plastics testing was used, based on Commission Regulation 10/2011 [2], combined with a untargeted liquid chromatography – high resolution mass spectrometry (LC-HRMS) workflow.

For the use in prior workflow, databases of chemicals of concern, regulatory and non-regulatory FCM substance lists were retrieved. The corresponding compound Chemical Abstract Service Registry Numbers (CASRN) were processed through a modified cheminformatics workflow "MS-Ready" [3] in an open-source KNIME Analytics platform to obtain the molecular descriptors used for the suspect screening search in the FCM extracts. Additionally, the obtained molecular descriptors were used to perform a toxicological profiling of potential hazardous compounds identified in the samples.

The obtained LC-HRMS data combined with a novel untargeted screening workflow enabled by Compound Discoverer 2.1. software allowed an accurate annotation of the identified compounds using the obtained FCM molecular descriptor database, online monoisotopic mass databases (ChemSpider, PubChem), publicly available curated fragmentation spectra databases (MassBank) and in-silico fragmentation matching (MetFrag, FISh).

References:

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EXPERIMENTAL STUDIES OF SOLID SOLUTIONS FORMATION IN THIOXANTHONE/XANTHONE BINARY SISTEM

CIETO ŠĶĪDUMU VEIDOŠANĀS EKSPERIMENTĀLIE PĒTĪJUMI TIOKSANTONA/KSANTONA DIVKOMPONENTU SISTĒMAS

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Organic solids are able to form very wide range of crystalline structures of different compositions – polymorphs, solvates, co-crystals and solid solutions. Both geometric and chemical aspects, such as molecules dimensions, form, symmetry, and intermolecular interactions, are important in understanding solid state properties of all the phases. In last decade while analyzing solid solutions and their molecular packing more and more attention is paid to geometric/stereochemical aspects, such as molecule chirality and configuration. The general aim of this research is to identify possible factors which could be used in prediction of the formation of solid solutions between chemically similar molecules and rationalize the formation or absence of the mentioned phase based on structural and energetic aspects.

In this research binary system of thioxanthone/xanthone has been studied in order to experimentally determine the information about formation of solid solutions followed by research of structural aspects contributing to the formation of solid solution.

Thioxanthone and xanthone were selected as model compounds because of their chemically similar structures, in which the different group doesn't significantly affect the dominant intermolecular interactions (Figure).

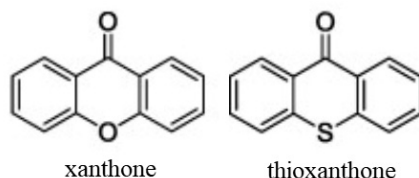


Figure. Molecular structures of thioxanthone and xanthone

Mixtures of thioxanthone/xanthone with compositions (0–100% with step size of 5%) were prepared and crystallized from chloroform. Powder X-ray diffraction and differential scanning calorimetry was used to determine and characterise formation of solid solutions in this system and based on the obtained results two-component phase diagram will be constructed. Computational studies have also been started, by employing that calculation of total unit cell energy can explain why one structure is more favourable. Using this approach it is possible to simulate solid solutions with various compositions and find solubility limit of compound in each other by comparing the total unit cell energy, with simulated structures additionally allowing comparison of bond angles and bond lengths.

STRUCTURAL ASPECTS OF FORMATION OF SOLID SOLUTIONS IN DIFFERENT BENPERIDOL – DROPERIDOL PHASES

CIETO ŠĶĪDUMU VEIDOŠANĀS STRUKTURĀLIE ASPEKTI DAŽĀDĀS BENPERIDOLA – DROPERIDOLA FĀZĒS

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Benperidol and droperidol are neuroleptic pharmaceuticals used as antipsychotics. Both compounds have very similar molecular structures – the two are only different by the order of C-C bond in the central ring (piperidine ring in benperidol, tetrahydropyridine in droperidol).

It is known that benperidol forms five polymorphs (^BI – ^BV) and eleven solvates (the most stable being ^BS_{Me}, ^BS_{Et}, ^BS_{ACN}, ^BDH), but droperidol forms four polymorphs (^DI – ^DIV) and eleven solvates (the most stable being ^DS_{Me}, ^DS_{Et}, ^DS_{ACN}, ^DDH) [1]. In previous research in cross-seeding experiments it was observed that it is possible to obtain droperidol phases isostructural to the benperidol phases, which suggest on solid solution formation between both compounds.

In this research mixtures of both compounds were crystallized to test the solid solution formation (see Table) while computational calculations were carried out to identify structural aspects responsible for differences observed in solid solution formation in different phases.

Table. Experimentally obtained crystalline phases in benperidol – droperidol mixtures

Benperidol / droperidol %	Phase				
	Methanol solvate	Acetonitrile solvate	Ethanol solvate	Ansolvate	Dihydrate
0:100	^D S _{Me}	^D S _{ACN}	^D S _{Et}	^D II	^D DH
5:95	SS^DS_{Me}	SS^DS_{ACN}	SS ^D S _{Et} +SS ^B S _{Et}	SS ^D II+SS ^B II	SS^DDH
10:90	SS^DS_{Me}	SS^DS_{ACN}	SS^BS_{Et}	SS ^D II+SS ^B II	SS^DDH
20:80	SS ^D S _{Me} +SS ^B S _{Me}	SS^DS_{ACN}	SS^BS_{Et}	SS^BII	SS ^D DH+SS ^B DH
30:70	SS ^D S _{Me} +SS ^B S _{Me}	SS ^D S _{ACN} +SS ^B S _{ACN}	SS^BS_{Et}	SS^BII	SS ^D DH+SS ^B DH
40:60	SS ^D S _{Me} +SS ^B S _{Me}	SS ^D S _{ACN} +SS ^B S _{ACN}	SS^BS_{Et}	SS^BII	SS ^D DH+SS ^B DH
50:50	SS^BS_{Me}	SS ^D S _{ACN} +SS ^B S _{ACN}	SS^BS_{Et}	SS^BII	SS ^D DH+SS ^B DH
60:40	SS^BS_{Me}	SS ^D S _{ACN} +SS ^B S _{ACN}	SS^BS_{Et}	SS^BII	SS ^D DH+SS ^B DH
70:30	SS^BS_{Me}	SS^BS_{ACN}	SS^BS_{Et}	SS^BII	SS^BDH
80:20	SS^BS_{Me}	SS^BS_{ACN}	SS^BS_{Et}	SS^BII	SS^BDH
90:10	SS^BS_{Me}	SS^BS_{ACN}	SS^BS_{Et}	SS^BII	SS^BDH
95:5	–	–	–	SS^BI	–
100:0	^B S _{Me}	^B S _{ACN}	^B S _{Et}	^B I	^B DH

D – droperidol phase, B – benperidol phase, S_{Me} – methanol solvate, S_{Et} – ethanol solvate, S_{ACN} – acetonitrile solvate, DH – dihydrate, I, II – polymorphs, SS – solid solution.

References:

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GEOCHEMICAL AND PHYLOGENETIC FACTORS AFFECTING ACCUMULATION OF MACRO- AND TRACE ELEMENTS IN THREE NATURAL PLANT SPECIES

ĢEOĶĪMISKO UN FILOĢENĒTISKO FAKTORU IETEKME UZ MAKRO- UN MIKROELEMENTU AKUMULĀCIJU TRIJĀS DABISKAJĀS AUGU SUGĀS

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Until present it was widely believed that plants require no more than 17 mineral elements to complete their life cycles. Nowadays it is assumed that plants can also accumulate other elements that now are considered as nonessential and might play a certain role in some biological processes. Nevertheless, the relative needs of many plant species in different trace elements are poorly quantified yet. The effects of environmental situation in the rhizosphere soil on the element accumulation in the plants are also not well investigated.

The most important factors controlling element concentrations in plants are soil composition and taxonomical status of a particular plant. Experimental studies during last decades [1] showed an unexpected tendency: different taxonomic groups and even plant species that are very close in botanical classification are characterized by absolutely different capability of some nutrient or trace element accumulation capability even if they grow in the same soil. Distinction becomes more significant if we compare plants growing in different soils.

Based on above facts, it can be suggested that each plant species is able to elaborate a specific element composition, which reflects mostly plant nutrient requirements rather than nutrient availability in the soil. To prove it and evaluate both factor importance, a series of ICP-MS, TXRF and C, H, N elemental analyses was performed for three natural plant species and soil extracts.

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COOPERATIVE DEVELOPMENT OF A HANDHELD SPECTROMETER FOR RADIATION DETECTION IN THE CONTEXT OF THE ESTONIA-LATVIA “HADEDE” PROJECT

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The European Union Basic Safety Standards Directive (96/29/Euratom) has been revised to a new version (BSS Directive 2013/59/Euratom) which the EU countries have to comply with since 2018. The updated BSS sets out standards aiming to protect the health of workers, medical patients and general public against the radiation from a broadened range of sources. Member states have to ensure that an appropriate program to monitor the level of radioactivity in the environment must be in place. With this in mind, the HADEDE project is initiated to improve the radiation measurement technology using know-how already available but not yet combined in Estonia and Latvia. Application of electric Stirling coolers for cooling germanium detectors to cryogenic temperatures in radiation spectrometers allows to create a portable device for field applications without the need for bulky dewars with liquid nitrogen. Power consumption and weight of modern hand-held devices available on the market, are relatively large. This limits the duration of operation without recharging batteries and makes field applications suboptimal. The implementation of this project involves cross-border cooperation of experts in different technical fields to solve a practical problem that is essential to both countries.

The goal of project HADEDE is to establish a cooperation between two SMEs (1 – Estflow Consulting OÜ, Tartu, Estonia and 2 – Baltic Scientific Instruments, Riga, Latvia) to design and manufacture a next-generation hand-held spectrometer. The project will combine the benefits of computer modeling and simulation expertise available in Tartu, Estonia with the strengths of custom manufacturing and long term experience in detector technologies in Riga, Latvia. The target is to achieve improved cooling solution for the spectrometer based on the Stirling principle. To achieve this it is crucial to reduce heat losses in the vacuum chamber of cryostat with the germanium detector. This will allow the use of a low-power Stirling cooler, a major power consumer in the device. This also reduces the size and weight of the hand-held spectrometer and makes its application more comfortable.

The main activities can be divided into two groups: (i) modeling and simulation of the design and (ii) manufacturing of the prototype, testing and final assembly. State-of-the-art Computational Fluid Dynamics code will be used to analyse the heat transfer and cooling capabilities of the design. Rigorous testing will be performed to gain confidence in the validity of the model.

Acknowledgement: This work has been carried out within the project “Hand-held spectrometer design” (HADEDE) supported by the cross-border cooperation program Interreg V-A – Estonia–Latvia, co-funded by the European Regional Development Fund. This work reflects the views of the authors; the managing authority of the program is not liable for how this information may be used.

EVALUATION OF CRYSTALLIZATION CONTROL IN PREPARATION OF NITROFURANTOIN HYDRATES

KRISTALIZĀCIJAS KONTROLES NOVĒRTĒJUMS NITROFURANTOĪNA HIDRĀTU IEGŪŠANĀ

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Nitrofurantoin (NF) is an antibiotic used to treat bladder infections. Studies have shown that it exists in two polymorph forms α and β [1], two monohydrates H I and H II where H I is thermodynamically less stable [2], multiple solvates, salts and co-crystals [3, 4]. Although both hydrates are prepared in similar way [2] there is lack of information describing conditions affecting formation of given hydrates.

NF was crystallized from multiple mixtures of water and organic solvents with and without additives to try to find and identify factors affecting phase obtained in crystallization and provide possible information on crystallization control.

Formation of pure metastable hydrate H I was observed only by crystallizing from water and acetonitrile mixture with a volume-to-volume ratio of 0.5. It was concluded that higher water concentration leads to hindering of formation of H I and facilitates the formation of H II instead. Addition of polymers in some cases inhibits the formation of H I but mostly leaves little to no effect on the obtained phase. With solvent exchange method obtained phases showed that if possible solvate is formed first, and if the water concentration is sufficient, hydrate is formed afterwards. Also, if solvent molecules in the solvate are bounded with NF similarly as water molecules in hydrate H II, interference leads to formation of H I.

Crystallization control possibilities were also evaluated by using quantum chemical calculations to investigate the association of NF and additive molecules and calculate Gibbs energy of association. Despite the fact that calculated energies suggested existence of possible stable associates between the additive and NF, the presence of these additives in crystallization process showed no detectable effect.

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RESEARCH ABOUT PHOSPHORUS, SULFUR AND NITROGEN DETERMINATION IN LICHENS

PĒTĪJUMS PAR FOSFORA, SĒRA UN SLĀPEKĻA NOTEIKŠANU ĶĒRPIJOS

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Lichens (*Lichenes*) belong to the group of symbiotic organisms which consist of two components: fungi and algae. They absorb water and nutrients directly from the air and therefore, they are sensitive to the air pollution, especially SO₂ is considered as the most hazardous substance which may negatively affect the population of lichen species.

The aim of our research was to analyse the content of phosphorus, sulphur and nitrogen in lichens and in respective soil.

Lichens samples (on the ground and on trees) were collected in 3 different locations in Balvi and Viļaka districts, with a distance of 10–30 km between them:

- the area of the former Kuprava drain pipe factory (Kuprava parish);
- the area of the former landfill (Kubuli parish);
- the Sita forest (Kubuli parish).

When choosing lichens sampling sites, it was important to verify the impact of the former Kuprava drain pipe factory, which operated during the period from 1971–1992 and used the Kuprava deposits for the production of drain pipes, ceramic pebbles and bricks. Those times surrounding area was covered with clay dust and mazut which was intensively used as a fuel.

Lichens samples dried at 105 °C degrees, ashing at 500 °C degrees in the muffle and the ashes were dissolved in 2M HCl. The air-dried soil samples were extracted in 0.2M HCl and 1% potassium alum.

The phosphorus content in lichens and soil was determined photometrically with ammonium molybdate. The sulfur content was determined as a sulfate ion with turbidimetry. For determination of total nitrogen in lichens, The Kjeldahl method was also applied.

The research results show that on the lichens collected from the leafy trees (*Xanthoria parietina*) phosphorus content is ~1.3 g·kg⁻¹ irrespective of their growing site (the former drain pipe factory, forest, or landfill). At the distance of 25 km from the factory, phosphorus content on the ground grown scrub lichens (*Cladina rangiferina*) decreases approximately twice (from 0.9 g·kg⁻¹ to 0.5 g·kg⁻¹). Sulfur content in lichens (*Cladina rangiferina*) in the Balvi and Viļaka districts is almost the same ~0.3 g·kg⁻¹.

When determining the amount of phosphorus in lichens collected at the former drain pipe factory (*Peltigera collina*), the increment of the phosphorus content was observed depending on the lichens growth site according to the following order: land → tree → stone or 0.9 g·kg⁻¹ → 4.0 g·kg⁻¹ → 7.7 g·kg⁻¹.

The analysis of soil samples shows a correlation between the content of phosphorus, sulfur and nitrogen in the soil and in the lichens from the same areas – as the concentration of these elements in the soil increases, similar changes are observed in the concentration of these elements in the lichens.

THE EFFECT OF THE USE OF WOOD ASH ON METALLIC ELEMENTS CONTENT IN THE FOREST FLOOR, SOIL, AND BLUEBERRIES (*VACCINIUM MYRTILLUS*)

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The aim of our research was to analyze the influence of wood ash on metallic elements content in the forest floor, soil and blueberries.

Samples of blueberries, soil and forest floor for quantifying the chemical content of metallic elements were collected from three different sampling plots. The first sampling plot was fertilized with bottom ash in February 2018, but the second and third plots were fertilized with fly ash in February 2017. Three tons of wood ash were used for the area of one hectare.

Blueberry (*Vaccinium myrtillus*) samples were collected at the end of August and in early September 2018. The samples of soil and forest ground were collected at the end of October 2018. Soil samples were collected in two depth layers: 0–10 cm and 10–20 cm. After collecting, the samples of soil and forest floor were air-dried.

The unwashed blueberries were dried at 50 °C and mineralized in the mixture HNO₃:H₂O₂ (6:2) using the closed microwave digestion system. The concentration of the elements in the sample solutions was determined by ICP-MS.

The air-dried and sieved soil samples were extracted in 1M HNO₃ solution. The concentration of metallic elements was determined by TXRF and as the internal standard was used gallium standard solution. The ash was dissolved in conc. HNO₃ and the forest floor samples were ashed in muffle at 550 °C. The concentration of metallic elements was determined by TXRF.

The results show that the cadmium content in the first sampling plot fertilized with bottom ash is about 1.5 times higher values than in the second and third sampling plot cases fertilized with fly ash. The content of other metallic elements in blueberries from controlled and fertilized plots is similar.

The content of determined elements in the soil samples has no noticeable differences between the controlled and fertilized sampling plots. It was found that the concentration of metallic elements determined in the soil samples doesn't exceed the maximum permissible limits, defined by the Regulations No 804 of the Government of the Republic of Latvia.

In the first plot, the concentration of manganese in blueberries and soil samples was higher than in other sampling plots. The peaty soil collected in the first plot had similar content of nickel, zinc, strontium and lead in different depth levels. The content of copper was higher in the layer of depth 10–20 cm. In the second sapling plot, it was determined that the content of manganese, nickel, and lead is higher on all levels of depth in comparison with other plots.

Acknowledgement: This work was supported by Short term scientific mission organized in scope of project "Research program on improvement of forest growth conditions 2016–2021" No 5-5.5_000z_101_16_31

ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE – ALTERNATIVE ROUTE ACHIEVING ENERGY SUSTAINABILITY

ELEKTROĶĪMISKA OGLEKĻA DIOKSĪDA REDUCĒŠANA – ALTERNATĪVA ILGTSPĒJĪGA ENERĢIJAS CIKLA NODROŠINĀŠANAI

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Carbon dioxide is a waste product and a source of environmental pollution. Researchers all around the world are looking for financially viable route to produce some valuable products [1]. Electrochemical CO₂ reduction is attracting attention due to the fast development of alternative electricity producing. Various catalysts are promising for variety of products from methanol to ethylene. Cu-based nanocatalysts have demonstrated to be applicable for selective methane, ethylene and ethane production with reasonably high efficiency [2]. However, the most efficient cell construction should still be developed. Early studies were carried out using classical electrochemical cell with a liquid electrolyte (water and non-water environment, specifically ionic liquids). The reduction reaction might take place from the gas phase or the carbon dioxide is dissolved in electrolyte. The role of electrolyte is not well understood. Recently also the all-solid cells analogous to the fuel cell are tested [1]. Such cells will typically use gas electrodes. In both cases, the ion conducting polymer material is used: a) to form the membrane separating anolyte from catholyte; b) as a binder for catalyst; c) for separating the gas phase from the liquid.

In this research, the sulfonated poly (ether ether ketone) polymer membranes are studied as a potentially suitable for “green chemistry” reactors. By combining the polymer with various filler materials (such as ionic liquids, inorganic oxides, graphene) and forming composites the research is focused on promoting overall catalytic electrochemical CO₂ reduction reaction.

Funding from European Union’s Horizon 2020 Research and Innovation Programme project under grant agreement No 768789 is greatly acknowledged.

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THE IMPACT OF FERTILIZER USED IN LEAF TREE PLANTATIONS ON HEAVY METAL CONTENT IN BIRCH BOLETE (*LECCINUM SCABRUM*)

LAPU KOKU STĀDĪJUMOS IZMANTOTĀ MĒSLOJUMA IETEKME UZ SMAGO METĀLU SATURU PARASTAJĀS BĒRZUBEKĀS (*LECCINUM SCABRUM*)

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Planting of *Populus tremula x tremuloides* is not very popular because of high risk of browsing. Aspens as an agricultural crop for biomass production – long term tree planting – short rotation coppice (SRC) are not a widespread crop in Latvia. The area where *Populus spp.* are planted as SRC has significantly increased since 2009 when support for energy wood crops growing was implemented. Now the area of *Populus* SRC has reached 250 ha. Aspens are also used for afforestation of agriculture land. In 2011, when the studied experimental plot was established, only 30 ha were afforested by aspens, while just 14 ha of aspens were planted as SRC. Soil amendments used in public forests and SRC plantings must not contaminate the soil and foodstuffs, such as mushrooms. Use of commercial fertilizers is not economically viable in all cases.

Fertilizers analyzed in this work are byproducts of industrial processes, such as digestate (waste matter of obtaining methane from manure), wood ash (waste product of central heating) and treated sewage sludge (byproduct of municipal water treatment systems). Long term effects of aforementioned fertilizers on heavy metal content in soil and mushrooms were studied in this work. Fertilizers were used once, during the tree planting in 2011. Soil and mushroom samples were collected seven years after the planting. Mushroom samples were prepared using microwave digestion and analyzed with Agilent 8900 Triple Quadrupole ICP-MS. Soil extracts were analyzed, using TXRF. Results are shown in Table.

Table. Heavy metal content in soil and mushroom samples (mg/kg)

Sample	Cr	Mn	Ni	Cu	Zn	Sr	Sn	Pb	As
Mushroom	0,07±0,02	5,0±0,5	0,26±0,04	26±4	31±5	0,5±0,2	<0,05	0,046±0,011	0,18±0,03
Soil	3,6±0,7	150±40	0,5±0,2	1,2±0,2	4,1±1,3	8,9±1,5	17±9	4,0±0,4	0,8±0,4

The preliminary results show no statistically significant differences between heavy metal content in differently fertilized and not fertilized soil samples, as well as mushrooms grown in this soil. Heavy metal content does not exceed the limits specified in soil quality standards [1].

Acknowledgement: This work was supported by Short term scientific mission organized in scope of project "Research program on improvement of forest growth conditions 2016–2021" No 5-5.5_000z_101_16_31

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ORGANISKĀS ĶĪMIJAS SEKCIJĀ

DDQ MEDIATED ELECTROCHEMICAL CLEAVAGE OF THE PARA-METHOXYBENZYL PROTECTING GROUP

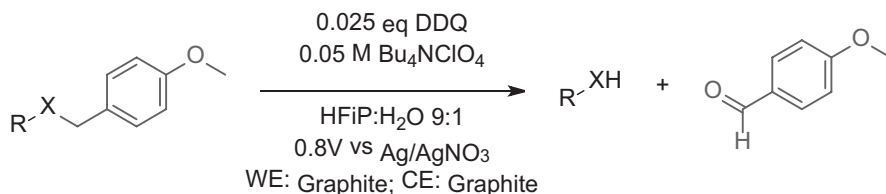
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Para-methoxybenzyl (PMB) group is a protecting group, widely used in organic synthesis for the protection of alcohols, carboxylic acids, and nitrogen containing compounds [1, 2]. The most common synthetically used methods for removal of the PMB protecting group involve stoichiometric amounts of strong oxidants, such as DDQ or CAN, or employ strong acids, such as TFA. Other methods have also been reported [1, 3, 4].

Deprotection of alcohols by means of DDQ is an easy and relatively cheap method, however, it is rather slow and employs multiple equivalents of DDQ, resulting in poor atom efficiency. What's more, DDQ hydrolyses in water, releasing toxic HCN gas [5]. The use of organic electrochemistry, on the other hand, can help to alleviate these issues. As a method, it is innately scalable, features high chemoselectivity and functional group tolerance [6]. This led to the exploration of the electrochemical approach to cleavage of the PMB protecting group.



Scheme. Electrochemical cleavage of the PMB protecting group

A novel synthetic method for deprotection of PMB ethers was developed (Scheme), using a mixture of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) and water as a solvent and a catalytic amount of DDQ, significantly reducing amounts of the toxic reagent necessary. As an electrode material, the commercially available and inexpensive graphite was used. The scope of the reaction was also explored, applying it for different substrates, the most notable of which are aromatic PMB ethers, electrochemical deprotection of which previously has not been reported.

Supervisor: Prof. Dr. E. Suna

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ELECTROCHEMICAL TRANSFORMATIONS OF FURFURYL ALCOHOL DERIVATIVES

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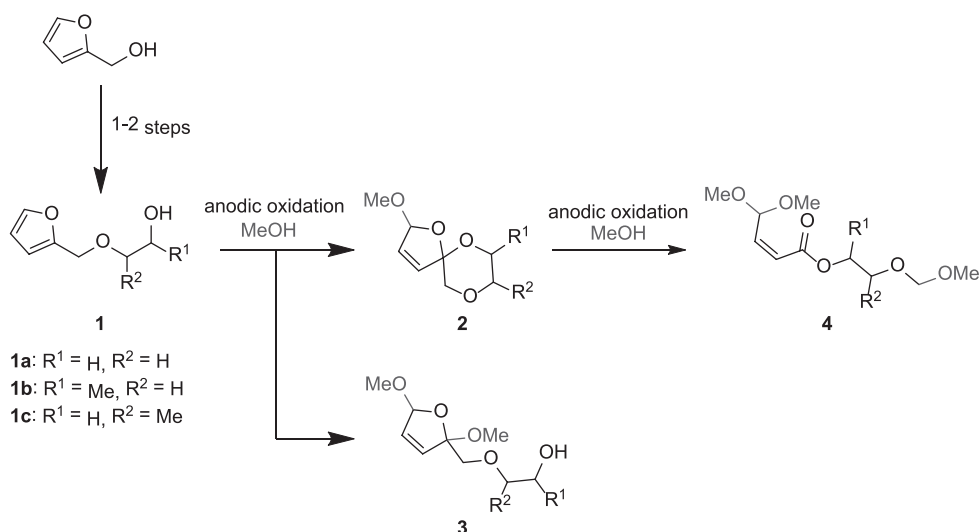
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Biomass is renewable, yet unexplored, source of small organic molecules [1]. Chemical conversion of biomass yields a number of simple furan derivatives – hydroxymethylfurfural, furfural and furfuryl alcohol – making them easily available and cheap building blocks to synthesize more complex molecules [1].

Previously, we have investigated electrochemical transformations of furfuryl alcohol derivatives with the focus to obtain spirocyclic compounds *via* intramolecular cyclization in the presence of methanol. Spirocyclic compound **2** was observed when intramolecular nucleophile in a substrate **1a** was a hydroxy group attached to the furan ring by a carbon linker. However, during the electrolysis, we also noted that the spirocycle **2** undergoes rearrangement to α,β -unsaturated ester **4**.

Our current work focuses on developing reaction conditions leading to efficient formation of α,β -unsaturated esters **4** from furfuryl alcohol derivatives **1a-c**.



Supervisors: prof. Aigars Jirgensons, Mg. chem. Anna Lielpētere

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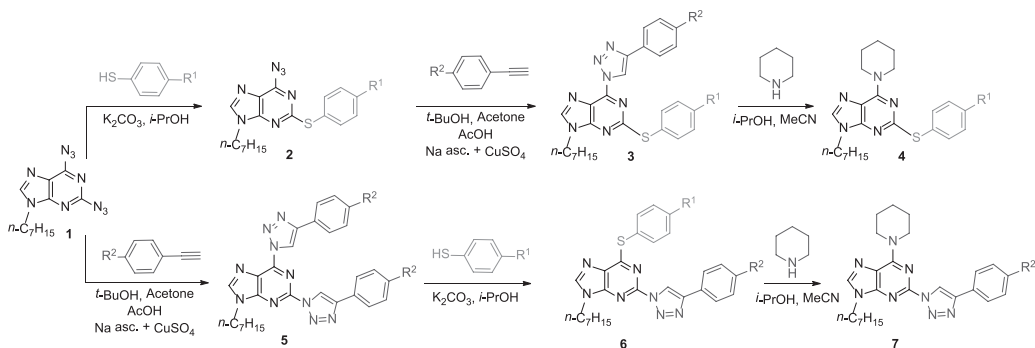
SYNTHESIS OF PHENYLTHIOPURINE DERIVATIVES

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Purine derivatives are widely studied due to their biological activity and extensive potential in medicine. Thiopurine based compounds have already been proven as effective tools in the treatment of cancer and autoimmune disorders [1].

A new synthetic approach for the synthesis of 6-azido-2-arylthiopurine derivatives **2** was developed. The optimized reaction conditions (*i*-PrOH solution) provided 2-arylthioderivatives **2** with good yields up to 74% [2]. Further CuAAC reaction led to 6-triazolyl-derivatives **3** with excellent yields up to 98%. Additionally, by rearranging the synthetic approach regioisomers **6** were obtained with yields up to 83%. Products **3** and **6** exhibited different NMR and UV absorbance data. Despite the location of triazolyl- and thiogroups following nucleophilic substitution with piperidine was observed at C6 position of purine (products **4** and **7**).



Product	R ¹	R ²	Yield, %
2a–2d	H, Cl, Br, <i>t</i> -Bu	–	50–74
3a–3h	H, Cl, Br, <i>t</i> -Bu	H, <i>n</i> -Pr	69–98
5a–5b	–	H, <i>n</i> -Pr	50–60
6a–6h	H, Cl, Br, <i>t</i> -Bu	H, <i>n</i> -Pr	62–83

This work was supported by the Latvian Council of Science grant No LZP-2018/2-0037.

Supervisor: Dr. chem. Ē. Bizdēna

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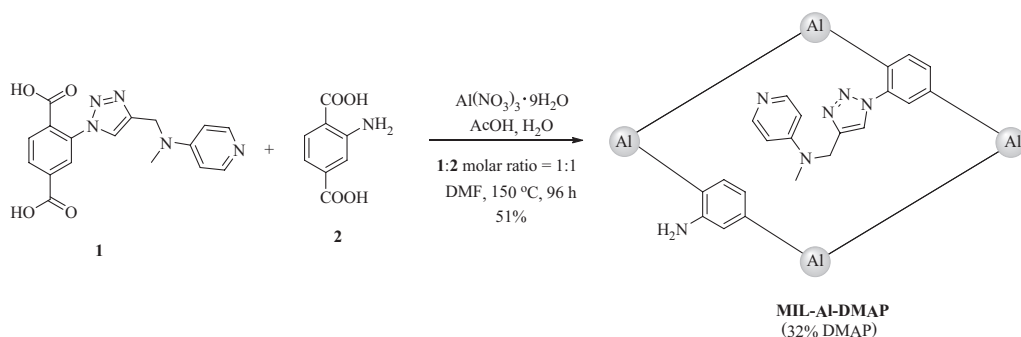
SYNTHESIS OF 4-DIMETHYLAMINOPYRIDINE EMBEDDED METAL-ORGANIC FRAMEWORK

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Metal-organic frameworks (MOFs) are coordination polymers formed by an extended network of metal ions (or clusters) coordinated to multidentate organic molecules [1]. Tunable porosity, surface area, and modular inorganic/organic hybrid structure of the MOFs offer opportunities to control the shape selectivity, regioselectivity, and enantioselectivity of reactions. Therefore, catalytically active MOFs with coordinatively unsaturated sites or bonded catalytically active species are extensively studied [2–3]. 4-Dimethylaminopyridine (DMAP) is a common nucleophilic catalyst that has already been embedded in a MOF structure. Unfortunately, due to coordinative attachment of DMAP molecule to MOF, most of the reported catalysts are not suitable for repeatable use [4–5]. To overcome this problem, alternative DMAP containing MOF structure was designed. It was found that MIL-53(Al)-NH₂ and MIL-101(Cr)-NH₂ MOFs were suitable for DMAP attachment. *De novo* MIL-Al-DMAP synthesis from DMAP **1** and BDC-NH₂ **2** was crucial to obtain chemically and structurally stable solid-state catalyst for alcohol acylation.



Supervisor: Prof. E. Suna

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CYSTEINYL- AND SELENOCYSTEINYL INDOLES AND BENZO[B]FURANES

Sindija Lapčinska

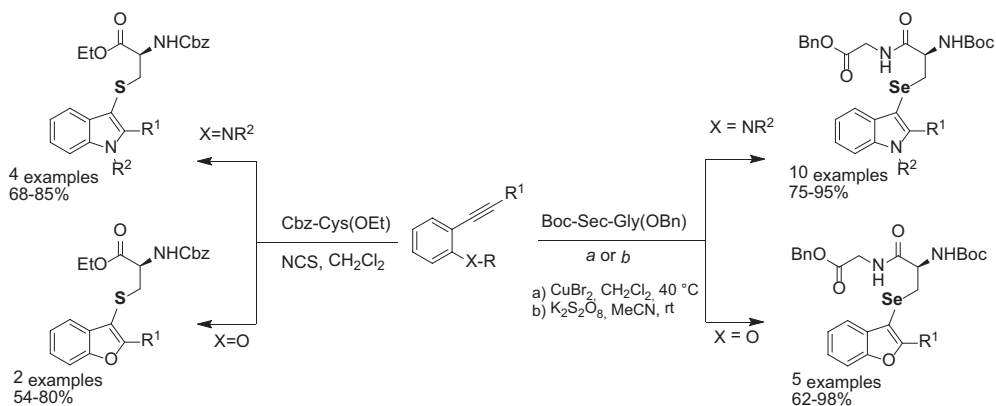
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Selenocysteine (Sec) is the 21st proteinogenic amino acid which is present in several important enzymes such as glutathione peroxidase, iodothyronine deiodinase, thioredoxin reductase and selenophosphate synthetase. Despite intensive studies of Sec in nucleophilic substitution reactions no any protocol was published so far using selenocysteine electrophile generation.

Recently we developed a new copper(II) bromide mediated method for the generation of selenium electrophile from diselenides. We expanded this approach to generate selenium electrophile in Sec containing peptides. Electrophilic species were further trapped in reaction with 2-alkynylanilines leading to the formation of 3-selenylindoles via 5-*endo*-dig mechanism. We also applied utilization of inorganic oxidants in purpose to obtain electrophilic Se-reagent. Thus, several examples of 3-selenylindoles were prepared in good to excellent yields (75–95%). Analogously, 3-selenylbenzo[*b*]furanes were obtained from the corresponding 2-alkynylphenols and 2-alkynylanisoles (62–98%).

Method was developed for preparation of 3-sulfenylindoles 3 as well. A novel electrophilic sulfur reagent – cysteinyl chloride was *in situ* generated from cysteine using NBS. Electrophilic sulfur species reacted with 2-alkynylanilines, 2-alkynylphenols and 2-alkynylanisoles yielding 3-sulfenylindoles and 3-sulfenylbenzo[*b*]furanes in good yields (68–85%).



Supervisor: Dr. chem. P. Arsenyan

OVERCOMING AGGREGATION CAUSED QUENCHING BY CATION- π INTERACTIONS [1]

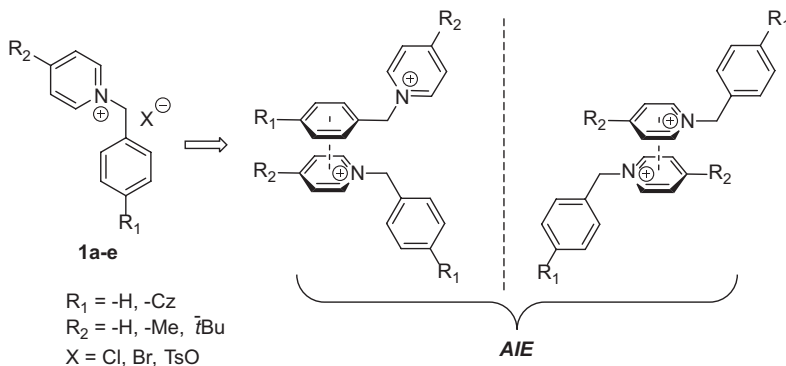
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Purely organic luminophores have been studied extensively due to their use in displays, artificial lighting, sensors etc. Photoluminescence quantum yields (PLQY) near unity had been achieved in solutions, however efficiency of organic luminophores is hampered by the loss of emissive properties in the solid state. This undesired feature is known as aggregation caused quenching (ACQ). The main cause for ACQ is the non-emissive intermolecular energy transfer between luminophores that usually proceeds through π - π interactions. Among various solutions to overcome this problem, introduction of steric bulk or anionic moiety in the proximity of π -system is most frequently employed. Nevertheless, strategies that help to avoid ACQ, require synthetic manipulations of the luminophores, often at the cost of their emissive properties and molecular simplicity.

This flaw of planar organic luminophores has resulted in the development of new strategies to achieve solid state emission. Most prevalent of such strategies are the aggregation induced emission (AIE) [2] and thermally activated delayed fluorescence (TADF) [3] phenomena. Luminophores benefiting from TADF and AIE are either highly twisted or exceedingly substituted. As such, TADF and AIE materials are synthetically challenging to obtain, which translates in higher costs. Obviously, a robust method of achieving high solid state PLQY in simple, easily accessible, conjugated and planar luminophores should be sought after. It is presented how π^+ - π and π^+ - π^+ interactions in **1a-e** can achieve high PLQY in the solid state.



Supervisor: Dr. chem., Prof. Edgars Suna

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ULTRALONG PURELY ORGANIC PHOSPHORESCENCE VIA INTRAMOLECULAR INTERACTIONS

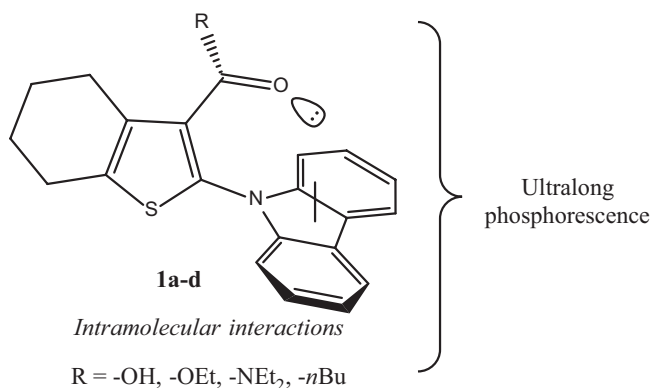
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Purely organic phosphorescent materials have attracted considerable attention because of their uses in artificial lighting, bio-imaging, data security, etc. Recent breakthroughs in the design of purely organic phosphorescent material have been achieved by the restriction of molecular motion via rigidification in polymer matrices or by intermolecular interactions, such as C—H...O, C=O...H, C—H...X (X=F, Cl, Br, I), C—H... π hydrogen bonds [1], lone pair- π and π - π interactions [2]. Successful was also the use of crystallization-induced phosphorescence (CIP) [1]. Materials possessing CIP characteristics can show ultralong lifetimes ($\tau_p > 0.1$ s) in the crystalline state.

To overcome the unpredictability of intermolecular interactions in the crystal lattice for phosphorescence generating close contacts we have designed and synthesized thiophene derivatives **1a-d**. The compounds feature a spatial proximity between the carbonyl group and carbazole subunit. In these designs, electron pair of the carbonyl group is forced to interact intramolecularly with carbazole π -system. Gratifyingly, thiophenes **1a-d** demonstrate ultralong phosphorescence regardless on the nature of substituent R, thus highlighting the importance of interactions between lone pair and aromatic π -system.



Supervisor: Dr. chem., Prof. Edgars Sūna; M.S. chem. Kaspars Leduskrasts

References:

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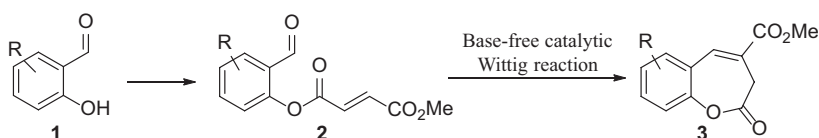
REVIEW ON WITTIG REACTION. SYNTHESIS OF BENZOXEPINONE DERIVATIVES

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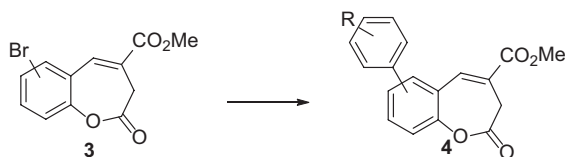
The Wittig reaction between carbonyl compounds and phosphonium ylides is one of the most important and most effective method for the formation of C=C double bond. The classical Wittig reaction suffers from several drawbacks: formation of phosphine oxide in equimolar amount; necessity of a strong base to generate phosphine ylide; the substrate must be compatible with basic conditions [1, 2].

O'Brien et al. described the first phosphine catalyzed Wittig reaction. Werner et al. developed first base-free catalytic Wittig reaction. Products of the intermolecular base-free catalytic Wittig reaction are succinates, but the intramolecular reaction gives benzoxepinones [2, 4]. Benzoxepinone derivatives were synthesized in two steps: acylation of 2-hydroxybenzaldehyde derivatives **1**, followed by the intramolecular base-free catalytic Wittig reaction [4].



Scheme 1. Synthesis of benzoxepinones

Bromine atom contained benzoxepinones were further converted to aryl-derivatives **4** by Stille and Suzuki reactions.



Scheme 2. Synthesis of aryl-derivatives of benzoxepinones

Supervisor: Dr. chem. A. Grandāne

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CATIONIC REARRANGEMENT REACTIONS OF PROPARGYL SILANES

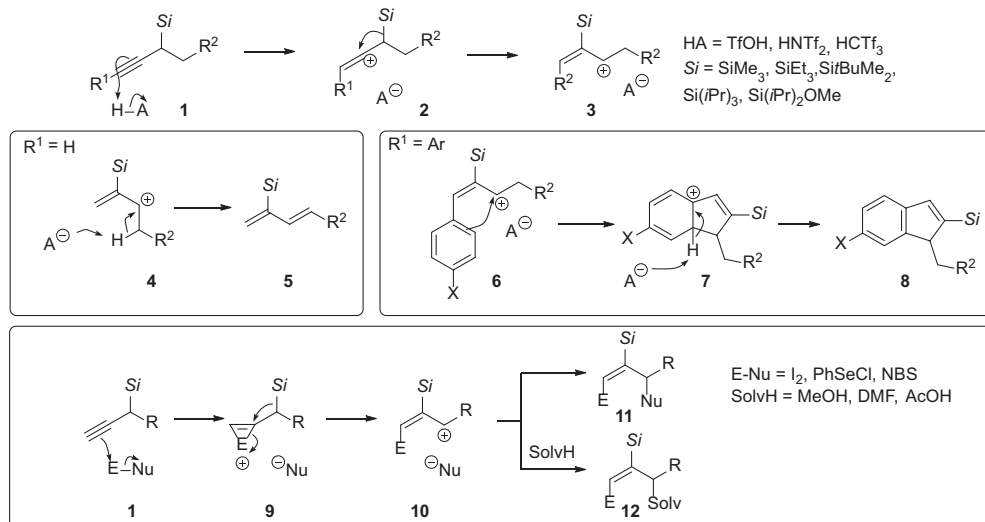
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Hosomi-Sakurai type reactivity of propargyl silanes towards electrophiles has been well documented. In some cases, 1,2-silyl shift in the intermediate β -silyl vinyl carbenium ion has been observed [1]. Here we report the generation of allyl carbenium ions from propargyl silanes by electrophilic activation. Three reactivity pathways are operational. Deprotonation to give silyl dienes, intramolecular cyclisation to give silyl indenenes and intermolecular addition to give allyl functionalized vinyl silanes.

Protonation of the triple bond of propargyl silanes with strong Brønsted acids results in formation of allyl carbenium ions **3** (Scheme 1). If $R^1 = H$, deprotonation gives silyl dienes **5**. In aryl substituted carbenium ions **6** both deprotonation and intramolecular attack to give silyl indenenes **8** can occur. Selectivity is influenced by polarity of the solvent, electronic properties of aryl substituents and the Brønsted acid used.

Activation of the triple bond with electrophilic halogen reagents results in allyl carbenium ions **10**. Addition of the conjugate nucleophile gives allyl functionalized vinyl silanes **11**. If a nucleophilic solvent is used, formation of vinyl silanes **12** is observed.



Scheme 1. Electrophilic activation of propargyl silanes.

Supervisor: prof., Dr. chem. M. Turks

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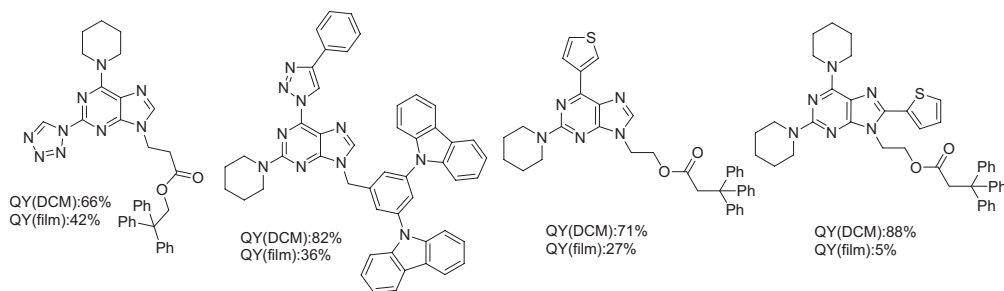
SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF FUNCTIONALIZED PURINE-HETEROCYCLE CONJUGATES

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Earlier we reported the synthesis of fluorescent 6-triazolyl purine nucleosides [1] and the synthesis of 2/6-triazolyl purine derivatives with amorphous groups at *N*(9) position. Different electron-donor and electron-acceptor groups were introduced in the purine structure that changed the fluorescent properties, while the trityl group increased amorphous properties [2] and carbazole groups enhanced hole transport capabilities [3].

In this work, the synthetic routes for introduction of azole electron-acceptor and amine electron-donor groups at purine *C*(2), *C*(6) and *C*(8) positions were designed. Purine *N*(9) position was functionalized with substituents with trityl or carbazole moieties. The fluorescent properties were studied in the solutions and in the films. Quantum yields in DCM reached up to 88% and up to 45% in the films.



Acknowledgements: This work was supported by ERDF project Nr. 1.1.1.1/16/A/131. Dr. K. Traskovskis and Dr. A. Vembris are acknowledged for the photophysical measurements and calculations.

Supervisor: Dr. chem. M. Turks, Dr. chem. I. Novosjolova

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1-ALKYL-1,2,3-TRIAZOLE MOIETY CONTAINING ARYLMETHYL MELDRUM'S ACIDS

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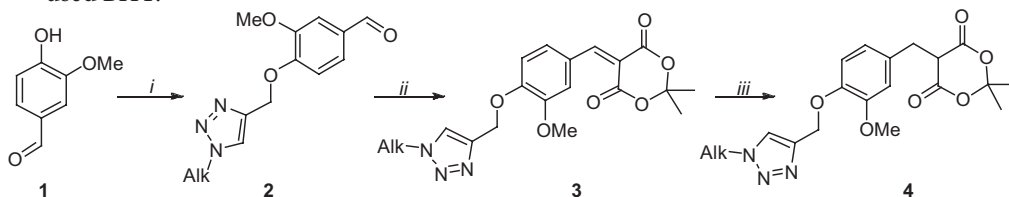
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Arylmethyl Meldrum's acids are found as excellent antioxidants both in lipophilic and hydrophilic media [1]. Although, the solubility for most of them is acceptable, some of the most active representatives are not soluble enough in vegetable oils and their derivatives. Thus, in order to improve both the solubility and activity of them additional research is developed. Herein, we present our results on compounds with long alkyl chains, which are attached to arylmethyl Meldrum's acid through 1,2,3-triazole linker.

The following route was recognized as the most appropriate for the synthesis of target compounds: hydroxyl group in vanillin (**1**) was alkylated and the aldehyde functionality was protected with acetal group. Further, 1,3-bipolar cycloaddition was used to convert alkyne to 1,2,3-triazole **2**. Knoevenagel condensation between aldehyde **2** and Meldrum's acid lead to arylidene derivative **3**. Treatment of the last ones with NaBH₄ gave target compounds **4**. Azide AlkN₃ was obtained from long chain saturated and unsaturated alcohols. Additionally, application of vegetable oils in the synthesis of antioxidants was evaluated.

The antiradical activity of the compounds **4** was determined by DPPH test. The antioxidants **4** showed nearly 3-fold higher antiradical activity than commercially used BHT.



i) propargyl bromide, KI, K₂CO₃, acetone, rf, 5 h 2) HO(CH₂)₃OH, PTSA, toluene, rf, 12 h 3) AlkN₃, NaAsk, CuSO₄·5H₂O, *t*-BuOH:H₂O (1:1), 60°C, 8-24 h ii) Meldrum's acid, piperidine, AcOH, toluene, 60°C, 12-36 h iii) NaBH₄, AcOH, CHCl₃, -5°C...rt

This work has been supported by the European Regional Development Fund within the Activity 1.1.1.2 "Post-doctoral Research Aid" of the Specific Aid Objective 1.1.1 "To increase the research and innovative capacity of scientific institutions of Latvia and the ability to attract external financing, investing in human resources and infrastructure" of the Operational Programme "Growth and Employment" (No. 1.1.1.2/VIAA/1/16/039).

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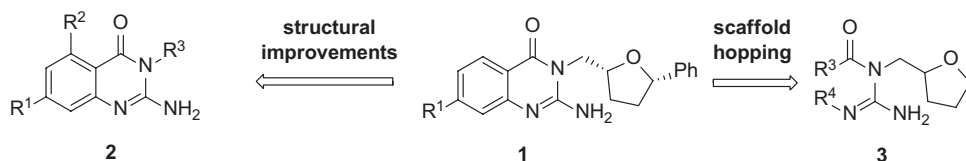
SYNTHESIS OF PLASMEPSIN INHIBITORS

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Malaria is a life threatening infectious disease caused by *Plasmodium* parasites and is transmitted by the bites of mosquitos [1]. The spread of drug-resistant malaria [2, 3] has urged the search for new anti-malarial agents. At the beginning of the project, NMR-based fragment screening with subsequent enzymatic assays showed that 2-aminoquinazolin-4(3*H*)-one scaffold possesses high inhibition of plasmepsins (malarial aspartic proteases) – enzymes which cause symptoms in malaria patients due to their protein-degrading activity. Thus, structures **1** were synthesized as perspective leads for antimalarial drug development [4].

Using molecular modeling and structural improvements of quinazolinone fragment, we obtained new active structures **2** with IC₅₀ up to 27 nM with improved selectivity to Cathepsin D (human aspartic protease) by installing polar groups (R²) in the 5-position [5] as well as evaluated the opportunity of modification of 3-position.



In parallel, we applied scaffold hopping approach to find new active inhibitors. Several compounds **3** were prepared to maintain the guanidine fragment as crucial element for the formation of hydrogen-bonding interactions with catalytic Asp34–Asp214 dyad. Unfortunately *N*-acetyl guanidines and 2-aminopyrimidin-4(3*H*)-ones of these series were found to be weak plasmepsin inhibitors, however the promising results demonstrated pyridopyrimidinones being active plasmepsin inhibitors and selective to Cathepsin D.

Supervisor: Dr. chem. D. Rasina

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LIQUID SULFUR DIOXIDE – BENEFICIAL SOLVENT FOR TRANSFORMATIONS INVOLVING CARBENIUM ION INTERMEDIATES

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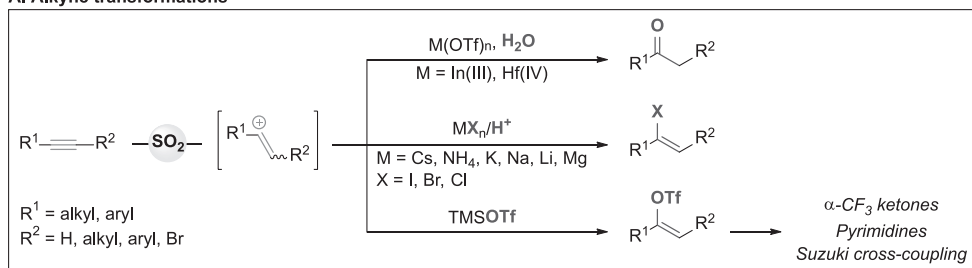
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Due to its high polarity and Lewis acid properties liquid sulfur dioxide can be used as a strongly ionizing solvent. Consequently, it has promoting effect on various organic transformations that involve ionic intermediates [1–4].

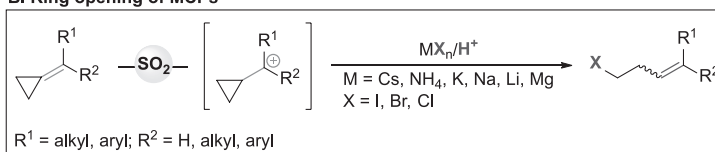
We have developed novel conditions for alkyne transformations through vinyl cation as an intermediate (A). The latter can be captured by nucleophiles like water, halide or triflate ion leading to the corresponding ketones, vinyl halides or vinyl triflates, respectively.

Recently, we have also discovered that similar conditions to alkyne hydrohalogenation can be used for ring opening of differently substituted methylene cyclopropanes (MCPs) to obtain β -haloalkenes (B).

A. Alkyne transformations



B. Ring opening of MCPs



Supervisor: prof., Dr. chem. Māris Turks

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SYNTHESIS OF ENANTIOMERICALLY PURE STEREOISOMERS OF (5-ALKYLPYRROLIDIN-2-YL) BENZYL ALCOHOLS

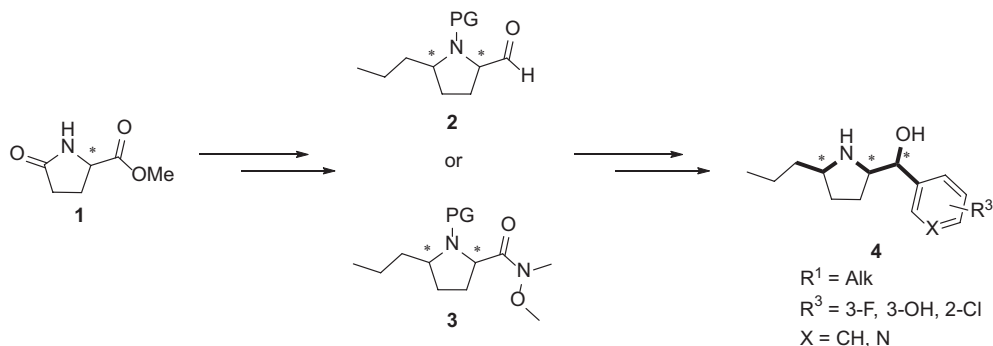
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β -Amino alcohol motif is found in many biologically important compounds with natural and synthetic origin, as well as in ligands and auxiliaries for asymmetric synthesis [1]. Locking conformation of the active fragment in bioactive molecules may increase the potency and selectivity towards target receptor, as well as improve metabolism. Therefore, our main focus was the synthesis of β -amino alcohols in which the motif is combined with a pyrrolidine cycle. With three possible stereocenters in target compounds **4**, the main goal of our work was to develop a method for the synthesis of all possible stereoisomers.



Our strategy towards target compounds started with (*R*)- or (*S*)-pyrroglutamate **1** which in 5–7 steps was transformed into aldehyde **2** or Weinreb amide **3**. Diastereoselective introduction of the propyl group was crucial to ensure *cis*- or *trans*-configuration relative to the existing stereocenter. In further transformations target compounds **4** were obtained as mixture of *syn*- and *anti*-diastereomers, which were successfully separated and identified.

The two routes, i.e., starting from aldehyde **2** and Weinreb amide **3**, were studied and compared in terms of selectivity and efficiency.

Supervisor: Dr. chem. I. Mutule

References:

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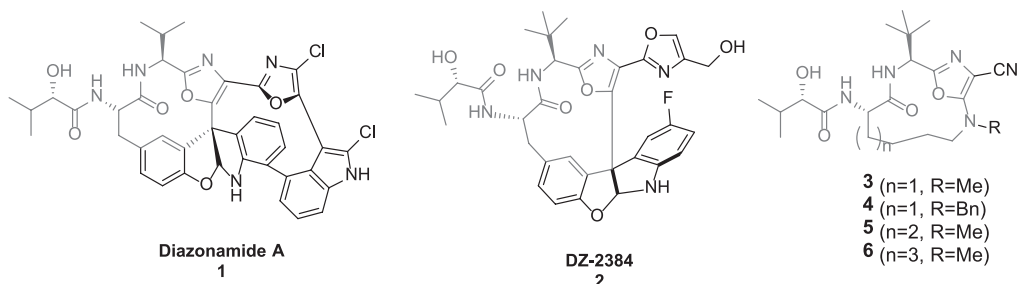
SYNTHESIS OF SIMPLIFIED ANALOGS OF DIAZONAMIDE A

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Diazonamides are a structurally unique class of secondary metabolites first isolated by Fenical and coworkers from the colonial marine ascidian *Diazona angulata* [1]. Diazonamide A (**1**) was found to be highly efficient anticancer agent with $IC_{50}=57$ nM [2]. Studies conducted by Harran [3] revealed that **DZ-2384** (**2**), a structurally simplified analog of **1**, is more potent ($IC_{50}=0,47$ nM) and it longer survives in the bloodstream. However, **2** still remains structurally complex and it's preparation requires many synthetic steps with poor overall yield.



Herein we report the synthesis of macrocycles **3–6** as simplified analogs of **DZ-2384**. Synthetic route towards macrocycles **3–6** uses ring closing metathesis as the key step.

Supervisor: Prof., Dr. chem. E. Suna

References:

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MILD METHODS FOR SYNTHESIS OF 6-AZIDO-2-SULFONYLPURINE DERIVATIVES

Jānis Miķelis Zaķis*, Kristers Ozols

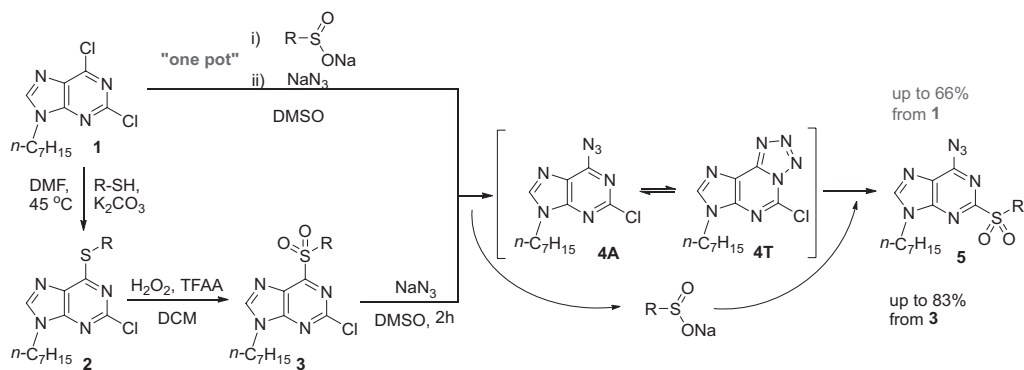
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Purine derivatives are widely studied due to their biological properties and application in medicine. Thiopurine derivatives are already being used in treatment of cancer and autoimmune disorders [1].

We have observed a sulfonyl group dance when substrate **3** was treated with NaN_3 . The transformation which lead to product **5** can be explained by azido-tetrazolo tautomerism. The latter activates purine cycle towards $\text{S}_{\text{N}}\text{Ar}$ reaction at C2. Reaction conditions were optimized and the best results were achieved using NaN_3 and DMSO at room temperature. Under these conditions sulfonyl group dance both with alkyl and aryl sulfones gave good yields.



R	Yield, % 3→5	Yield, % 1→5
4-Cl-C ₆ H ₅	83	54
C ₆ H ₅	77	66
c-C ₆ H ₁₁	47	49

Additionally, a simpler synthetic approach for the synthesis of 6-azido-2-sulfonyl-purine derivatives **5** was developed. The reaction was carried out using different sodium sulfinate salts and after the maximum conversion to substrate **3** was achieved, NaN_3 was added to the solution giving good yields of target product **5**.

Supervisors: Dr. chem. M. Turks, Dr. chem. I. Novosjolova

This work was supported by the Latvian Council of Science grant No LZP-2018/2-0037

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PEPTIDOMIMETIC MALARIA PLASMEPSIN INHIBITORS WITH IMPROVED SELECTIVITY AGAINST CATHEPSIN D

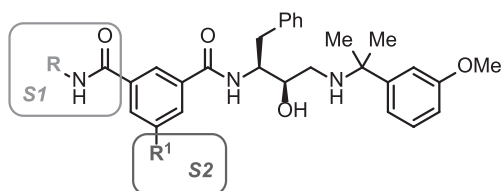
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Plasmodium falciparum is one of the four parasite species of *Plasmodium* that cause malaria in humans. The rapidly growing resistance of parasite has affected most of the anti-malarial drugs. The potential anti-malarial drug targets could be aspartic proteases (plasmepsins) – Plm I, Plm II, Plm IV that are found in the food vacuole of the parasite [1].



R and R¹ are selectivity inducing substituents

✓ Plm IV/Cat D selectivity up to 50-fold

✓ EC₅₀(Pf) = 6.0-0.3 nM

GlaxoSmithKline phenotypic screening hit was developed to generate hydroxyethylamine based plasmepsin (Plm) inhibitors exhibiting growth inhibition of the malaria parasite *Plasmodium falciparum* at nanomolar concentrations. Lead optimization studies were performed with the aim of improving Plm inhibition selectivity versus the related human aspartic protease cathepsin D (Cat D). Optimization studies were performed using Plm IV as a readily accessible model protein, the inhibition of which correlates with anti-malarial activity [2]. Guided by sequence alignment of Plms and Cat D, selectivity-inducing structural motifs were modified in the S1 and S2 sub-pocket occupying substituents of the hydroxyethylamine inhibitors. This resulted in potent anti-malarials with an up to 50-fold Plm IV/Cat D selectivity factor [3].

More detailed investigation of the mechanism of action of the selected compounds revealed that they inhibit parasite egress from erythrocytes [3].

Supervisor: Prof., Dr. chem. E. Sūna

References:

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