

PLENĀRREFERĀTI

ĶĪMIJAS nozarē

**COMPUTATIONAL CHEMISTRY AND SOLID-STATE NMR:
A MARRIAGE MADE IN HEAVEN***Paul Hodgkinson**Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK
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With the combination of magic-angle spinning for resolution and cross-polarisation for sensitivity in mid 1970s, solid-state NMR soon become established as a powerful tool for the identification of solid forms e.g. distinguishing polymorphic forms of the same compound. However, beyond some straightforward applications, it was difficult to extract detailed structural information from NMR spectra. Similarly, NMR parameters, such as relaxation times, are sensitive to dynamic processes, but it is often not obvious what dynamic processes are determining the relaxation times.

The advent of efficient DFT-based methods to predict NMR parameters has transformed this situation, allowing structure and NMR measurements to be directly related, giving rise to the developing field of "NMR crystallography" [1,2]. In this talk, some of the contributions the Durham NMR group has made to this field will be described, starting with examples from inorganic framework materials where NMR provides complementary information to XRD without the need for computation, to examples where computation is essential to identifying incorrect XRD solutions, and where molecular dynamics simulations are needed to understand NMR data.

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- [1] NMR Crystallography, Harris, R.K., Wasylishen, R.E., Duer, M.J., Eds.; Wiley, **2009**, 520 p.
[2] Mafra, L. *Solid State Nucl. Magn. Reson.* **2015**, *65*, 1 (Special issue on NMR crystallography).

DEVELOPMENT OF NOVEL NANOSTRUCTURED PHOTOELECTROCHEMICAL PLATFORM FOR CHEMICAL SENSING

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Electrochemical sensors are the most widespread types of analytical devices for monitoring of air and liquid environment. The recent problem of electrochemical sensors is to improve sensitivity of the device.

ZnO is well known material for sensing. The advantage of ZnO is a facility for low cost and simple route of fabrication of nanostructures. Based on our previous experience, one dimensional (1D) nanostructures showed higher sensitivity due to higher concentration of adsorption sites [1].

Therefore, combination of 1D nanostructures and electrochemical method could increase sensitivity of the device. The electrochemical response is related to current density, what is defined by the electronic properties of the sensitive layer. Photoexcitation of electrons could be another approach to enhance the sensor performance.

In the present work, 1D ZnO nanorods were grown by chemical bath method. Structure and optical characterization has been performed using Raman, SEM, reflectance and photoluminescence spectroscopy. Cyclic voltammetry measurements have been performed with light and dark conditions.

References

1. A. Tereshchenko, M. Bechelany, R. Viter, V. Khranovskyy, V. Smyntyna, N. Starodub, R. Yakimova, [Optical Biosensors Based on ZnO Nanostructures: Advantages and Perspectives. A Review](#), *Sensors and Actuators B: Chemical*, 229 (2016) 664-677

INTRA- AND INTERMOLECULAR TRANSFORMATIONS OF FUNCTIONALLY SUBSTITUTED ALKYNES

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Functionally substituted alkynes are versatile intermediates in organic synthesis [1]. Generally, π -acidic transition metal salts are used as catalysts for activation of triple bond and therefore subsequent cyclizations or skeletal rearrangement processes become possible [2]. This lecture will cover results of our recent investigations in the field of transition metal-free inter- and intramolecular transformations of functionalized alkynes. The following topics will be presented:

- Cyclizations of acetylenic aldehydes.
- Cycloisomerizations of nitro-alkynes.
- Transformations of functionalized propargylic substrates.

The mechanistic aspects of the reactions together with their scope and limitations will be discussed.

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- [2] (a) Shiroodi, R. K.; Gevorgyan, V. *Chem. Soc. Rev.*, **2013**, *42*, 4991. (b) Lauterbach, T.; Ganschow, M.; Hussong, M. W.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Adv. Synth. Catal.*, **2014**, *356*, 680. (c) Wang, L.-J.; Zhu, H.-T.; Wang, A.-Q.; Qiu, Y.-F.; Liu, X.-Y.; Liang, Y.-M. *J. Org. Chem.*, **2014**, *79*, 204. (d) Yang, W.; Hashmi, A. S. K. *Chem. Soc. Rev.* **2014**, *43*, 2941.

**ELABORATION OF INNOVATIVE FUNCTIONALIZED OR
CHEMICALLY MODIFIED MATERIALS AND CREATING OF NEW
ANALYTICAL METHODS****INOVATĪVU FUNKCIONALIZĒTU VAI ĶĪMISKI MODIFICĒTU
MATERIĀLU IZSTRĀDE UN JAUNU ANALĪTISKO PĒTĪŠANAS
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The 2016 was a year of important changes- the Department of Chemistry was transferred from historical building (Valdemāra 48) to the new university campus (Academic Centre for Natural Sciences, Jelgavas 1). The transfer included the updating of study programs and laboratory facilities. The research was reorganized as a part of university project “Nano, Quantum Technologies, and innovative materials for economics” (project leader Prof. D.Erts). It was planned to realize the project by 11 Department employees (1 Assoc. Prof., 1 docent, 1 leading scientist). The number of young employees was increased from 8 to 12 (including 1 leading researcher, 3 researchers, 7 PhD students and 1 research assistants). Also 14 BSc and 10 MSc students are doing research on project topics and under supervision of the project participants.

Table 1

Current research directions and research outcomes (in 2016).

Research directions	Publications	Conference presentations	BSc thesis submitted	MSc thesis submitted
1. Polymer nanocomposite membranes for application in alternative energy devices.	1	5	1	2
2. Ionic liquids as solvents and/or catalysts in organic synthesis.	2	1	1	1
3. Synthesis and research of crystalline organic solids as pharmaceutical active ingredients.	2	4	4	4
4. Innovative chemical analysis methods.	-	5	1	2
Together:	5	15	7	9

Main scientific results are following:

1. Studied polyetheretherketone sulfonation kinetics and elaborated the sulfonation degree analysis methods (titration, thermal analysis + IS, X-ray fluorescence). Impedance analysis of ionic liquid- lithium salt composition revealed that the 1,3-dimethylimidazolium dimethylphosphate and lithium nitrate electrolyte is thermally stable up to 170 °C and suitable for application in lithium-ion batteries [1].
2. For membrane applications optimized the synthesis of dimethylphosphate and acetate based ionic liquids. Both demonstrated good thermal and chemical stability. The β -alkyl aspartates as unsubstituted zwitterionic surfactants are prepared by the addition reaction of ammonia to alkyl maleates. The applicability of these materials is characterized by evaluation of their surface activity, toxicity and biodegradability. β -alkyl aspartates has been demonstrated as a highly biodegradable and almost nontoxic surfactants [2-3].
3. The main focus was on cocrystals as a way to improve the characteristics of materials (PhD thesis by Inese Sarceviča, 2016). The mechanochemical, thermal and solvent vapour-assisted cocrystallisation of aliphatic dicarboxylic acids (C3–C10) with isoniazid has been studied. It was revealed that the rate of mechanochemical and vapour assisted cocrystallisation depends on the acid chain length and shows alternation between odd- and even chain acids. The results of thermal cocrystallisation showed that the eutectic melting temperatures of isoniazid–dicarboxylic acid mixtures follow the same trend as the melting points of dicarboxylic acids. The synthesis and research of crystalline organic solids as pharmaceutical active ingredients included degradation kinetics of furazidin and crystallization of droperidol and benperidol [4-5].
4. Most interesting of developed chemical analysis methods are following. Isotope-ratio mass spectrometry (IRMS) was used to analyze the hydrogen isotopic composition in geological and biological objects. It was useful for characterization and mapping of food webs and seston in the Gulf of Riga and Eastern Baltic [6]. The developed analysis methods also allowed improving the synthesis of hydroxylapatites.

Summarizing the project results, the planned milestones are reached and project outcomes exceeded the planned. Large number of students, post-graduate students and young scientists are involved in research. The cooperation with different institutions has been established. The project participants were doing research in Gothenburg and Chalmers universities with support from Erasmus programme (E.Sprūģis). Study course Surface and Colloidal chemistry for MSc students has been prepared for 2017 in cooperation with Latvian Institute of Organic Synthesis (Assoc. Prof. G.Vaivars).

References:

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ORGANISKĀS ĶĪMIJAS SEKCIJA

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POLYPHENOL RICH EXTRACTS OF *CAMELINA SATIVA*

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Camelina sativa is an oilseed plant that belongs to the *Brassicaceae* family. Camelina press-cakes contain remarkable amount of glucosinolates, antioxidants, including polyphenolic compounds (394 mg GAE/100 g meal), tocopherols, vitamin C and carotenoids [1-3]. The phenolic content strongly depends on the oil extraction process [2].

In this work, extracts of press-cakes of *Camelina sativa* seeds as potential sources of antioxidants were studied. The press-cakes were extracted with different solvents under variable conditions. The obtained extracts were characterized by total polyphenol content (TPC) and 1,1-diphenyl-2-picryl hydrazyl (DPPH) and galvinoxyl (GO) radical scavenging activity. TPC was expressed as mg of gallic acid (Fig. 1), sinapic acid or chlorogenic acid per 100 g of press-cake meal. DPPH and GO inhibition was expressed as IC₅₀ values. The highest TPC (1536 mg GAE/100 g meal) was observed for 70% ethanol extract prepared at room temperature from defatted meal. Ethanol extract demonstrated the highest antiradical activity, when extraction was realized under reflux: extract of defatted meal was most active against DPPH (2 μg GAE/mL), but non-defatted meal - against GO (3 μg GAE/mL).

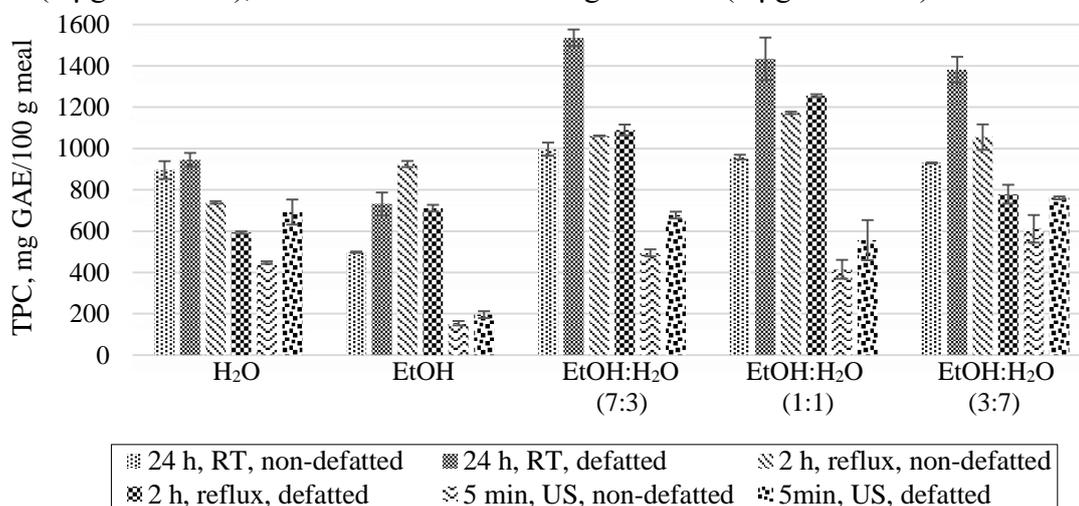


Fig. 1. Total polyphenol content of extracts of camelina seed press-cakes (RT - room temperature; US - ultrasound)

Supervisor: Doc. Inese Mieriņa, Prof. Māra Jure

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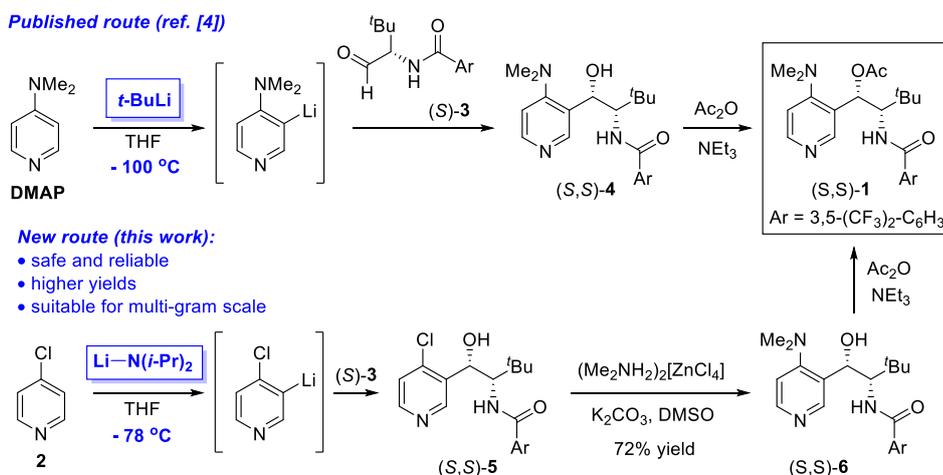
Simonas Balkaitis

DEVELOPMENT OF GRAM-SCALE SYNTHESIS OF CHIRAL DMAP CATALYST

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Ever since scientists noticed that DMAP accelerates acyl transfer reactions, a broad range of chiral DMAP analogues for asymmetric transformations have been synthesised by groups of Fu,^[1] Connon^[2] and Vedejs.^[3] Recently, development of a *tert*-leucine-derived chiral DMAP catalyst (*S,S*)-**1** for dynamic kinetic resolution of heterocyclic hemiaminals has been reported.^[4,5] The published milligram-scale synthesis of chiral pyridine (*S,S*)-**1**^[4] involves the use of highly pyrophoric *tert*-butyllithium reagent to install the chiral subunit in the pyridine core. We have developed considerably more safe and high-yielding alternative route for multi-gram scale synthesis of DMAP **1**.



I am truly grateful for financial support from Erasmus + program which supported me during the three months of traineeship in Latvia. Grant no. 2016-1-LT01-KA103-022877-12100-P76.

Supervisor: Prof. Edgars Sūna

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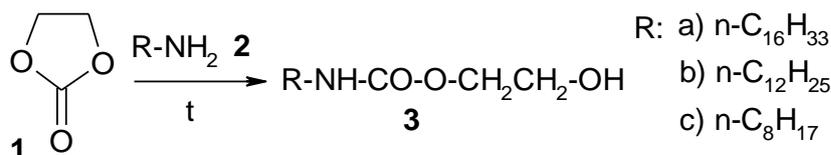
Sindija Brica

A SIMPLE ROUTE TO NON-IONIC SURFACTANTS

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Surfactants can be found among the most widely spread man-manufactured substances in the world, and they are produced in millions of tons per year. Very strict regulations are in place for their utilization/exploitation and production. They should not only be highly efficient in washing and cleaning processes but also practically non-toxic, sufficiently biodegradable and reasonably cheap to make their application favorable to people. Various methods are elaborated for production of modern surfactants, both chemical and enzymatic [1-5] allowing the preparation of anionic, cationic, zwitterionic and non-ionic surfactants, useful for different applications. Prices of reagents and the degree of complexity of their preparations together with the biological properties of these surfactants quite frequently limit exploitation of such surfactants. Therefore, the elaboration of a straightforward method for the synthesis of non-ionic surfactants is discussed in this communication.



Recently we have found that a simple acylation reaction of primary alkyl amines (**2**) with ethylene carbonate (**1**) at reasonably high temperature (~ 150°C) results in the formation of promising nonionic surfactants – N-alkyl carbamates with hydrophobic alkyl group at nitrogen atom and N-H and O-H bonds in the hydrophilic parts of the surfactants (**3**).

Supervisor: Prof. Andris Zicmanis

References:

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Ance Eglīte*, Linda Pudnika

SYNTHESIS OF ALIPHATIC ETHERS USING DICATIONIC AND MONOCATIONIC ACIDIC IONIC LIQUIDS

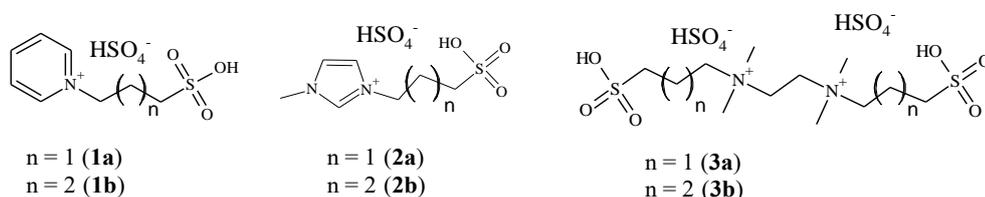
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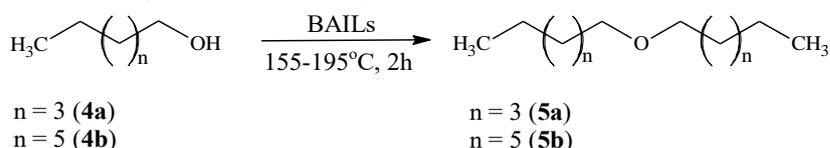
Ionic liquids are new class of solvents and catalysts that have become attractive research targets in organic synthesis due to their unique physical and chemical properties, such as non-flammability, low vapour pressure, high thermal stability, low melting point, large liquid temperature range and rather simple adaptation for specific chemical tasks [1-3].

Brønsted acidic ionic liquids are used as alternative reaction media instead of traditional homogenous and heterogenous acids in various chemical processes and reactions: esterification, Biginelli reaction, etherification, cyclodehydration [1-3]. This research represents a different approach to synthesis of aliphatic ethers using both - monocationic and dicationic Brønsted acidic ionic liquids.

Monocationic pyridinium and imidazolium ionic liquids and dicationic tetramethylethylenediamine based acidic ionic liquids are synthesised in accordance with previously described methods [4].



Acidic ionic liquids are used for syntheses of long chain alkyl ethers. Analysing previously reported results in literature temperature and ratio of used reagents are optimized [3]. Optimization of parameters allows to reach higher conversion of 1-octanol and 1-hexanol and higher yields of dihexylether and dioctylether.



Supervisor: Asoc. Prof. Anda Prikšāne

References:

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Mantas Jonušis*, Indrė Misiūnaitė, Girius Kisielius

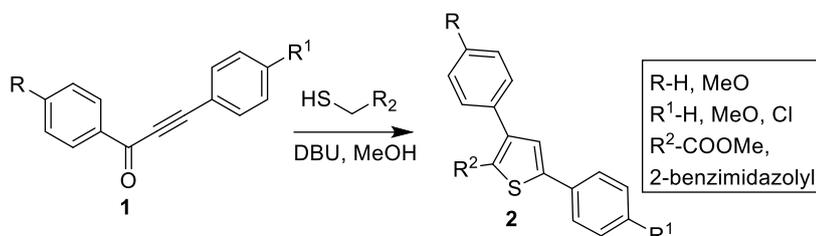
SYNTHESIS OF 3,5-DIARYL-2-SUBSTITUTED-THIOPHENES

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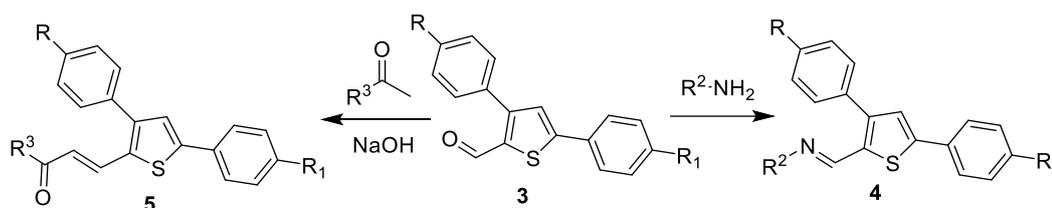
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Thiophene based compounds are widely explored and applied in pharmaceutical and physical fields of science [1]. Classical routes to thiophene synthesis are Gewald reaction and Paal-Knorr thiophene synthesis. Now days many other synthetical methods are developed towards the substituted thiophene synthesis [2].

We have synthesized series of 3,5-diaryl-2-substituted-thiophenes from 1,3-diarylprop-2-yn-1-ones **1** and active methylene group containing thiols.



Compounds **1** were synthesized in excellent yields from substituted phenylacetylenes and corresponding benzoyl chlorides in Et₃N as a base and solvent and CuI as a catalyst. Compounds **2** with R² = COOMe were reduced to alcohols using LiAlH₄ and oxidized to aldehydes **3** with PCC in DCM. Series of compounds **4** and **5** were derived from **3**.



Furthermore, previously unexplored products **2** with R² = 2-benzimidazolyl substituent exhibited fluorescent properties and good solubility in organic solvents, while thiophene derivatives **4** and **5** could potentially be applied as dyes and pigments.

Supervisor: Prof. Inga Čikotienė

References:

- [1] Rasmussen, S. C.; Evenson, S. J.; McCausland, C. B. *Chem. Commun.* **2015**, 51, 4528-4543.
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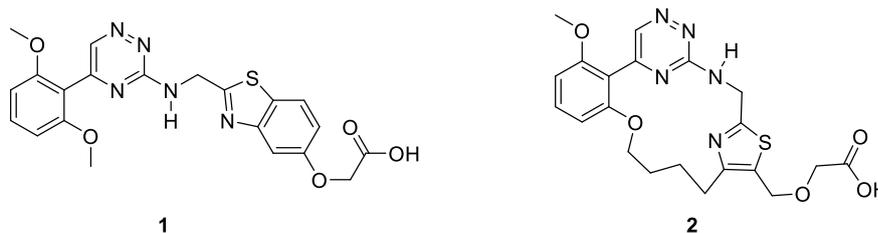
Toms Kalniņš

SYNTHESIS OF MACROCYCLIC ANTIMICROBIAL AGENT

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Increasing resistance of Gram-negative (G-) microorganisms to existing antimicrobial therapy is a serious threat to human health with potentially grave consequences [1]. Among various strategies to combat the resistance problem, one of the most promising is the combined therapy approach, where existing antibiotics are used together with potentiators. The latter help to shut-off or diminish resistance towards antimicrobial agents.

Recently a highly effective triazine-based potentiator **1** has been developed. Triazine **1** disrupts the synthesis of the outer cell wall of G- pathogens [2], thus facilitating transport of antibiotics through the double cell-walls. Molecular modelling studies have shown that macrocycle **2** has the potential to be even more efficacious. Herein we report synthesis of triazine containing macrocycle **2**.



Synthetic approach toward macrocycle **2** was based on separate synthesis of triazine and thiazole-containing building blocks followed by their assembly into macrocycle.

Supervisor: Prof. Edgars Sūna

References:

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ELECTROCHEMICAL SYNTHESIS OF HYPERVALENT IODINE MEDIATOR AND ITS APPLICATION IN THE SYNTHESIS OF SUBSTITUTED BENZOXAZOLES

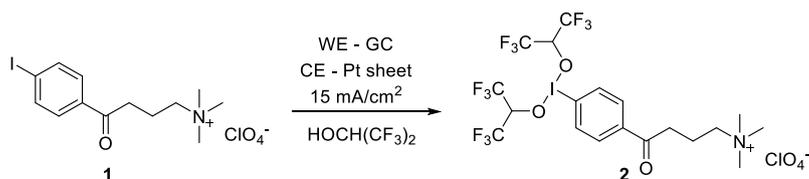
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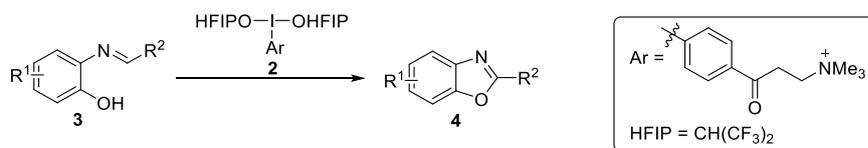
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Electroorganic synthesis is considered to be a useful method in organic synthesis. Electrochemical conversion of organic compounds can be used to avoid the usage of toxic or harmful reagents [1, 2]. Recently Francke developed electrochemical oxidation of iodine(I) mediator **1** (Scheme 1) [3]. The formed iodine(III) compound **2** was directly used in C-N and C-C coupling reactions.



Scheme 1. Electrochemical Generation of Iodine(III) Compound

To further explore reactivity of the electrochemically synthesized hypervalent iodine mediator **2** we, together with Francke's group, have developed the cyclization reaction towards substituted benzoxazoles **4** (Scheme 2). The scope of benzoxazoles was explored and differently substituted benzoxazoles were obtained in moderate to excellent yields.



Scheme 2. Iodine(III) Mediated Cyclization Reaction Towards Benzoxazoles

Supervisor: Prof. Edgars Sūna

References:

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Emilis Gudelis^{1,2}

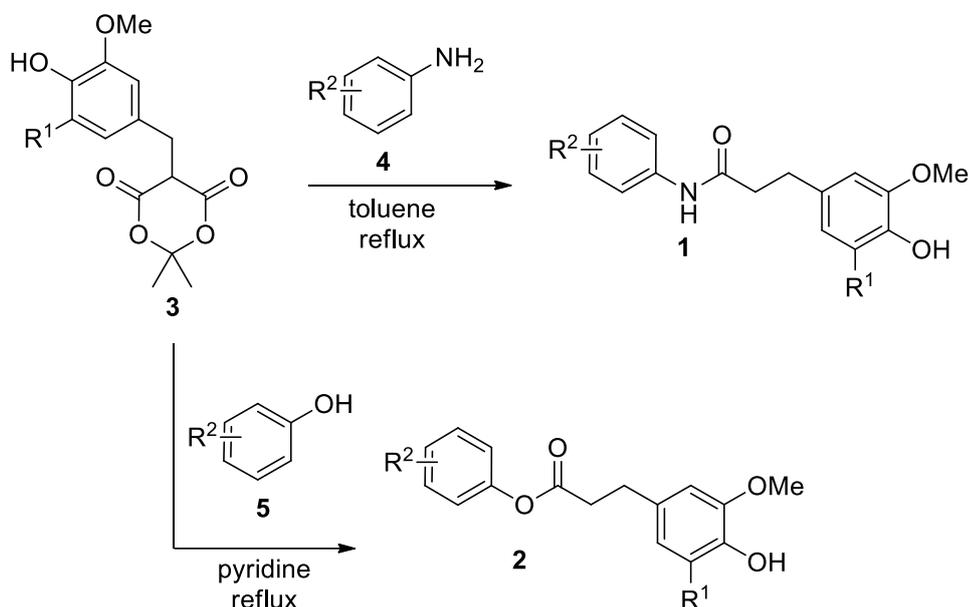
AMIDES AND ESTERS OF SUBSTITUTED DIHYDROCINNAMIC ACID AS ANTIRADICAL AGENTS

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Amides¹ and esters² of substituted cinnamic acids are well known antioxidants. Herein, we present our results on antiradical properties of partially hydrogenated cinnamic acid derivatives - anilides **1** and esters **2**. The target compounds **1** and **2** were obtained through cleavage of substituted Meldrum's acid **3** with aromatic amines **4** and phenols **5**, respectively. The antiradical activities of the synthesized amides **1** and esters **2** were analysed by 1,1-diphenyl-2-picrylhydrazyl and galvinoxyl tests. Several of the compounds **1** and **2** demonstrated better antiradical activity than *e.g.*, commercially widely used butylated hydroxytoluene.



Supervisors: Doc. Inese Mieriņa, Prof. Māra Jure

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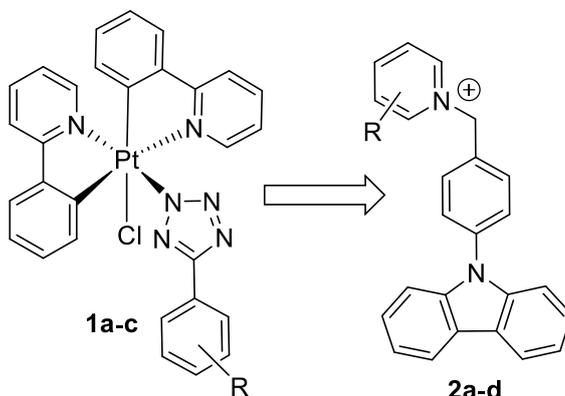
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AGGREGATION INDUCED EMISSION BY CATION- π INTERACTIONS

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Organometallic and purely organic luminophores have been studied extensively. Recent developments in the luminescence field have allowed for photoemission efficiency for purely organic emitters to exceed 25%. One of such developments is the aggregation induced emission (AIE). AIE results in higher quantum efficiency for luminophores in solid state as opposed to that in solutions. Importantly, AIE is fundamentally opposite to the undesired aggregation caused quenching (ACQ) phenomenon [1].

We have observed that cation- π interactions in Pt(IV) complexes **1a-c** can lead to AIE effect, hence allowing for increase of the solid state emission. The cation- π interaction was also successfully incorporated in the structure of purely organic luminophores **2a-d**, resulting in a strong AIE effect. Additionally, a significant loss in AIE intensity was observed in **2b** and **2d** where cation- π interactions were hindered by introduction of unfavourable steric effects.



1a, R = -4-CH₂NMe₃⁺

1b, R = -3-CH₂NMe₃⁺

1c, R = -2-CH₂NMe₃⁺

2a, R = -4-H

2b, R = -4-Me

2c, R = -4-*t*Bu

2d, R = -3,5-diMesityl

Supervisor: Prof. Edgars Sūna

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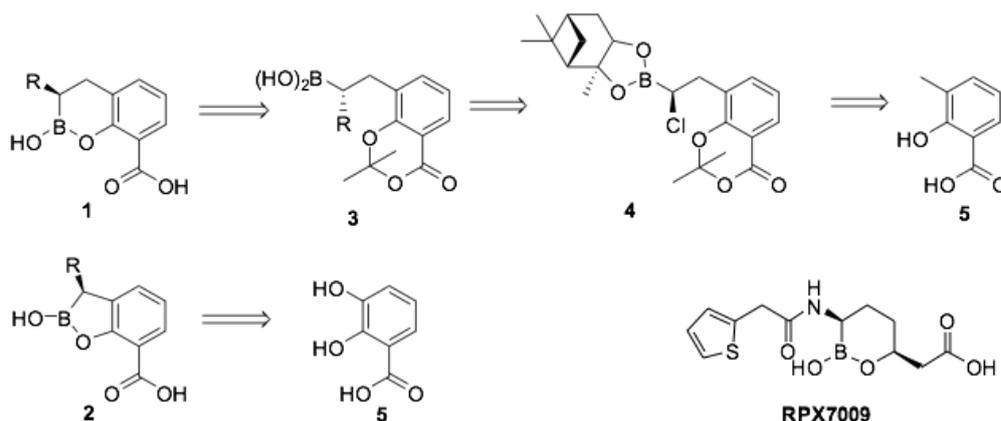
Anete Parkova

CYCLIC BORONIC ACIDS AS BETA-LACTAMASE INHIBITORS

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β -Lactamases enable resistance to almost all β -lactam antibiotics. Pioneering work revealed that acyclic boronic acids can act as ‘transition state analogue’ inhibitors of nucleophilic serine enzymes, including serine β -lactamases. The β -lactamase-catalysed hydrolysis of β -lactam antibiotics (BLAs) is of central importance in antibiotic resistance. Clavulanic acid is a β -lactam-based inhibitor of the class A serine β -lactamases (SBLs) and is widely used in combination with penicillins [1].

Since acyclic boronic acids are established as SBL/PBP (penicillin-binding-protein) inhibitors and the SBL inhibitor **RPX7009** is in clinical trials [2]), we have focused on the synthesis of cyclic boronic acids **1** and **2**.



Synthesis of cyclic boronic acid **1** starts with a protection of 3-methylsalicylic acid **5**, a bromination of methyl group with NBS, followed by Suzuki borylation with B_2Pin_2 and transesterification with (+)-pinandiol. Matteson’s homologation gives chlorinated compound **4**, which after S_N2 reaction with a nucleophile and deprotection of boronate in acidic conditions gives boronic acid **3**. To get the target compound **1**, conditions for deprotection of acetonide protecting group still has to be found.

Similar synthetic method was tried to get the cyclic boronic acid **2**.

Supervisor: Dr. chem. Pēteris Trapencieris

Acknowledgement: 7th Framework Programme project „Strengthening the research and innovative capacities of the Latvian Institute of Organic Synthesis, the leading Baltic regional centre for drug discovery” (InnovaBalt)

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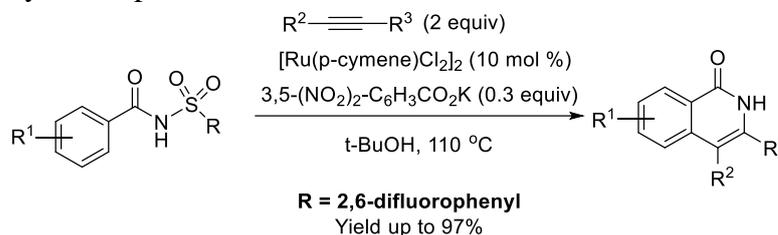
Elina Petrova

N-SULFONYLCARBOXAMIDE AS AN OXIDIZING DIRECTING GROUP FOR RUTHENIUM CATALYZED C-H ACTIVATION/ANNULATION

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Functionalization *via* C-H activation enables atom and step economic synthesis of the complex molecules and has motivated a considerable progress of method development in recent years [1]. An effective C-H activation methodology has provided new routes for the construction of the variety of heterocycles. Isoquinolone derivatives can be obtained by Ru catalyzed C(sp²)-H activation of amides followed by the annulation of the intermediate metallacycle with olefins or alkynes [2].

We have developed an efficient traceless method for the synthesis of isoquinolones by Ru catalyzed annulation of *N*-sulfonylcarboxamide with alkyne. In this reaction, *N*-sulfonylcarboxamide acts as both an internal oxidant and directing group. Catalyst re-oxidation takes place in the N-S bond cleavage step. Of all *N*-sulfonylcarboxamides studied, the most efficient was *N*-2,6-difluorobenzenesulfonamide which led to the formation of unstable sulfinate and readily decomposed to 1,3-difluorobenzene under the reaction conditions.



Supervisors: Dr. chem. Aigars Jirgensons, Dr. chem. Dace Rasiņa

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Mārcis Sējējs

TETRAZOLE HEMIAMINAL AS A CHIRAL AUXILIARY

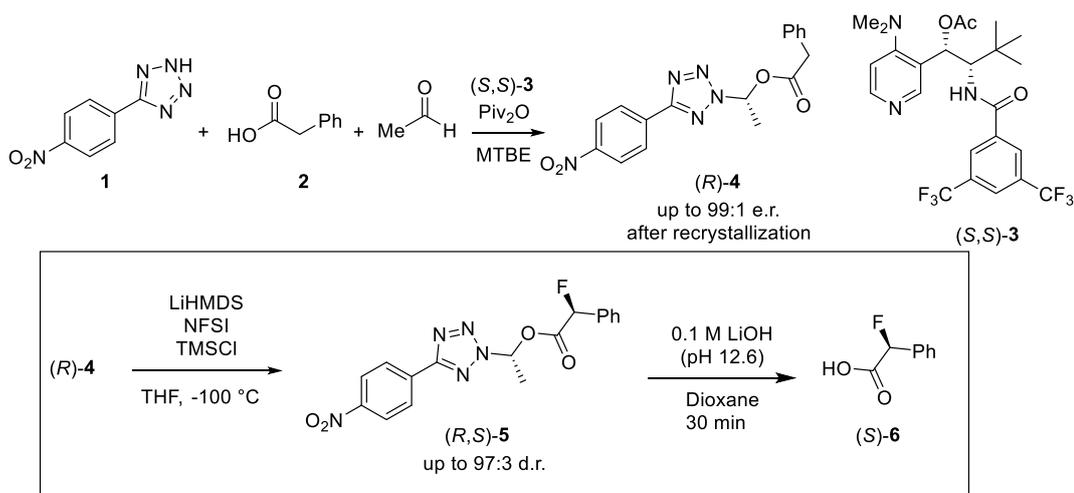
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Chiral auxiliaries are widely used in synthesis of enantioenriched molecules. Many of chiral auxiliaries require relatively harsh reaction conditions for removal after the diastereoselective synthesis step. Herein we report the use of tetrazole hemiaminal as easily accessible and removable chiral auxiliary for α -fluorination of carboxylic acid.

Chiral DMAP (*S,S*)-**3** catalysed dynamic kinetic resolution of tetrazole hemiaminals to afford enantiomerically pure hemiaminal (*R*)-**4** in a single step. [1] The obtained chiral ester (*R*)-**4** was successfully employed in α -fluorination of phenylacetic acid with excellent diastereomeric ratio (up to 97:3). It must be noted that the presence of TMSCl in the fluorination mixture is essential to ensure high diastereoselectivity. Importantly, removal of chiral auxiliary takes place under very mild conditions.



Supervisor: Prof. Edgars Sūna

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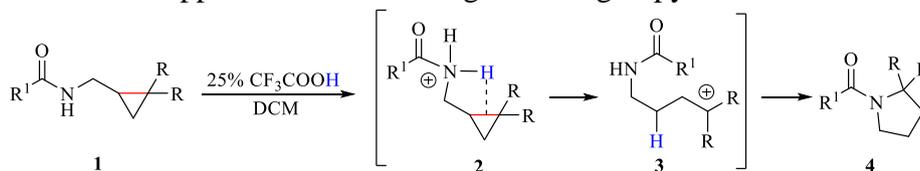
Marija Skvorcova

AMIDE GROUP DIRECTED PROTONOLYSIS OF CYCLOPROPANE. EN ROUTE TO 2,2-DISUBSTITUTED PYRROLIDINES

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Ring opening of cyclopropanes provides an unusual option for the functionalization of C-C bond. In literature, it is known that the cleavage of cyclopropane can be promoted by electrophiles such as Hg^{2+} , Pt^{2+} , Tl^{2+} , Pd^{2+} , Br^+ , H^+ , however, regioselectivity for the attack of the electrophile is difficult to achieve [1-4].

Herein we present directed protolytic cleavage of cyclopropane **1** in substrates **2** where protonated amide serves as an intramolecular proton donor. The resulting intermediate carbenium ion **3** is trapped with amide nitrogen leading to pyrrolidine derivatives **4**.



We have demonstrated that cyclopropanes with amide ($\text{R}^1 = \text{Ph}$, Me , ClCH_2), carbamate ($\text{R}^1 = \text{OEt}$) or urea ($\text{R}^1 = \text{NHPh}$) function can selectively direct the proton attack to cyclopropane C-C bond, while in the case of electron withdrawing amide ($\text{R}^1 = \text{CF}_3$) the cleavage was unselective. We have explored substrate scope ($\text{R} = \text{H}$, Ar , Alk) for the transformation of aminomethylcyclopropanes **1** to pyrrolidines **4** using carbamate function as a directing group.

Supervisor: Dr. chem. Aigars Jirgensons

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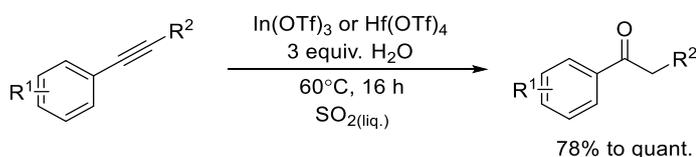
Krista Suta

ALKYNE HYDRATION AND HYDROHALOGENATION IN LIQUID SULFUR DIOXIDE

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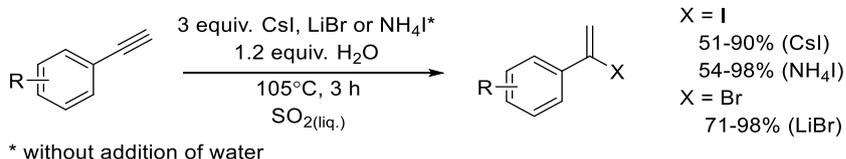
Sulfur dioxide is not only a useful building block in a synthetic organic chemistry but in its liquid state ($\text{SO}_{2(\text{liq.})}$) can be used as a strong polar solvent as well [1-3]. Herein we report a catalytic alkyne hydration and a new approach for the alkyne hydrohalogenation promoted by $\text{SO}_{2(\text{liq.})}$ as a reaction medium.

Hydration of alkynes is useful reaction for introduction of valuable carbonyl functionality. Nowadays, instead of the use of environmentally hazardous mercury salts, the main strategy for the alkyne hydration is the use of transition metal catalytic systems and acidic solvents or additives. Combination of In (III) or Hf (IV) triflate as a catalyst and $\text{SO}_{2(\text{liq.})}$ as a solvent allowed us to obtain desired arylketones in good to excellent yields without direct addition of acid (Scheme 1). Due to the medium effects the catalyst loadings can be reduced to less than 1 mol% for electron rich alkynes without loss in yields.



Scheme 1. Alkyne hydration in $\text{SO}_{2(\text{liq.})}$

Hydrohalogenation of alkynes is a straightforward strategy for synthesis of vinyl halides. Screening of ammonium and group 1 and 2 halides for reactivity towards phenylacetylene in $\text{SO}_{2(\text{liq.})}$ revealed that CsI, LiBr and NH_4I provided up to almost quantitative conversion of starting material into the desired vinyl halide. After optimization of the reaction conditions a series of aryl vinyl iodides and bromides were synthesized with moderate to excellent yields (Scheme 2).



* without addition of water

Scheme 2. Alkyne hydrohalogenation in $\text{SO}_{2(\text{liq.})}$

Supervisor: Prof. Māris Turks

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Aurelija Urbanaitė*, Lukas Šteinys

SYNTHESIS OF FUNCTIONALIZED 1,3-DIENES VIA ADDITION OF PRIMARY AMINES TO 2-(1-ALKYNYL)-2-CYCLOALKEN-1-ONES

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Electron-deficient 1,3-conjugated enynes possessing alkynyl, alkenyl and carbonyl functional groups are able to undergo nucleophilic addition reactions [1]. Typically 2-(1-alkynyl)-2-alken-1-ones participate in transition-metal catalyzed or electrophile-mediated tandem nucleophilic addition-cyclization reactions or cycloaddition-cyclization cascades obtaining polysubstituted furan derivatives [2]. Whereas there are only few publications about the synthesis of polysubstituted pyrroles from 2-(1-alkynyl)-alken-1-one oximes [3] or *in situ* formed imines of 2-(1-alkynyl)-alken-1-ones [4] in the literature. Keeping that in mind we decided to synthesize imines of 2-(1-alkynyl)-alken-1-ones and to investigate their cyclization reactions to polyfunctional pyrrole derivatives, but unexpectedly we found that electron-deficient 1,3-conjugated enynes react with primary aliphatic amines in a unique isomerization-addition manner.

Herein we describe mild and efficient synthesis of functionalized 1,3-dienes, which proceeds *via* regio- and stereoselective nucleophilic addition of primary aliphatic amines to 2-(1-alkynyl)-2-alken-1-ones with double bond migration.



$n = 1, 2$

$R = \text{Ph}, 4\text{-MeOC}_6\text{H}_4, 4\text{-FC}_6\text{H}_4, 4\text{-ClC}_6\text{H}_4, n\text{-Bu}$

$R' = c\text{-Hex}, t\text{-Bu}, n\text{-Bu}, i\text{-Bu}, i\text{-Pr}, c\text{-Pr}, \text{Bn}, \text{HC}\equiv\text{CCH}_2, \text{H}_2\text{C}=\text{CHCH}_2$

The scope and limitation of this unprecedented catalyst-free isomerization-addition reaction will be discussed.

Supervisor: Prof. Inga Čikotienė

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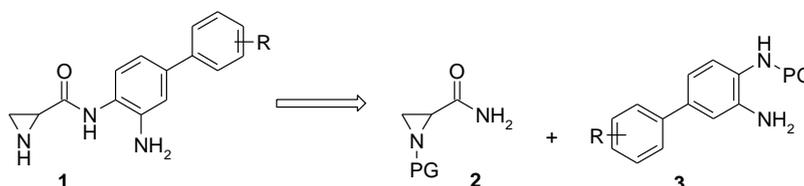
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*Diāna Zača***SYNTHESIS OF POTENTIAL EPIGENETIC ENZYME INHIBITORS***Latvian Institute of Organic Synthesis, Aizkraukles 21, Rīga, LV-1006, Latvia**e-pasts: shejla@osi.lv*

Epigenetic mechanisms have a key role in the control of biological processes, and chromatin alterations may lead to the onset and progression of many diseases. Histones go through different epigenetic modifications, including acetylation, methylation, phosphorylation, ubiquitination and others, more recently identified [1].

The zinc-dependent mammalian histone deacetylases (HDACs) catalyze the hydrolytic removal of acetyl groups from histone lysine residues. Overexpression of HDACs have been demonstrated to be involved in numerous types of oncologic and nononcologic diseases (neurological, inflammatory and viral pathologies). Therefore regulation of histone modifications is important in cell formation, differentiation and proliferation [2].

According to the computer modulation studies, we turned our interest to aziridine ring moiety in the scaffold of the structure potential HDACs inhibitors. Our synthetic aim was acylated o-phenylenediamines **1** and their synthesis started from N-substituted leakadine **2**. After its activation we have developed several synthetic schemes to reach desired regioselectivity for amino groups. Obtained activated amide in the aziridine series was involved in the reaction with synthesized monoprotected diamines **3** to form anilide. The subsequent deprotection resulted in the desired aziridine derivative (**1**; R=H).



HDAC inhibitory activity will be determined for the obtained compounds.

Supervisor: Dr. chem. Pēteris Trapencieris

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ANALĪTISKĀS un FIZIKĀLĀS
ĶĪMIJAS SEKCIJA

STRUCTURE OF NEW NUCLEAR BUILD PROGRAM IN EU COUNTRIES

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The structure of nuclear new build programs in EU countries are analysed with the U.K., Finland and Lithuania used as examples. Together with France, these are EU countries with advanced ambitions for nuclear new build. In the development of national nuclear programs, each country can consider the balance between electricity demand, current market price for electricity, and the costs of the electricity produced by the new build nuclear power plant that are higher than current market price for the electricity. Long term energy and electricity price and demand predictions so far have been unreliable, particularly in Eastern Europe, and this long-term uncertainty has to be taken into account when planning a very long term investment like NPP.

It is observed that the structure of the nuclear new build program depends on the size of the country. The UK program will use a government-based price guarantee: the contracts include a guaranteed strike price based on a difference scheme and with new state-owned company to act as a single counterparty to eligible generators [1]. Financing of Finnish nuclear power plants is done through the Mankala model, where energy producers are jointly owned by energy wholesalers, retailers, distributors, and large industrial companies that are obligated to buy the energy at the cost of production and are entitled to sell it to third parties. The owners are thus obligated to bear the costs of production [2].

Lithuania, in the Visaginas NPP project, plans to use a Special Project Company (SPC) that owns, develops, builds, runs and decommissions the NPP. It is expected that the SPC will be jointly owned by a strategic investor and the governments of all three Baltic States – Lithuania, Latvia, Estonia. The owners of the SPC will be obligated to purchase the electricity at production costs in proportion to their share in SPC [3]. This structure seems to be necessary in order to broaden the market basis that will support the future NPP, but it has an extra element of political complexity that has not been used before in NPP projects.

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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APPLICATION POSSIBILITIES OF ESR SPECTROSCOPY FOR ANALYSIS OF CARBON BASED DIVERTOR MATERIALS

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Carbon based materials, such as carbon fibre composites (CFC), are suitable for use in fusion devices as divertor and plasma facing materials due to low Z and good thermal conductivity. CFC is a divertor material in the JET configuration aimed to test materials for the International Thermonuclear Experimental Reactor [1] and is proposed as plasma facing material in the stellarator W7-X divertor [2].

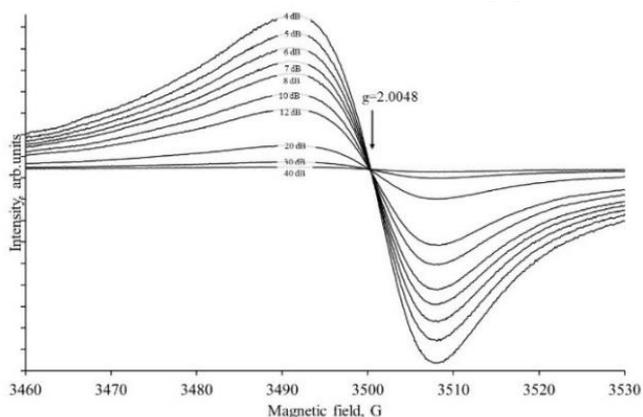


Fig. 1 Carbon fibre composite ESR spectra at different power

In order to understand the mechanisms taking place during plasma – wall interactions, it is important to identify the content of the erosion products and deposited layers, including types of possible paramagnetic defects.

An analysis of plasma non-exposed divertor materials with electron spin resonance spectroscopy (ESR) is performed to estimate the types of paramagnetic defects. In plasma non-exposed CFC an ESR signal with g-factor 2.0048 occur, probably due to presence of unpaired electrons in aromatic rings. The obtained results will be used for developing a data basis for identification of defects in divertor erosion products.

Acknowledgement:

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**STRUCTURE AND OPTICAL PROPERTIES OF GRAPHENE/ZnO
NANOLAMINATES**

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In the past few years zinc oxide (ZnO) and graphene (G) were intensively studied due to their unique physical properties. ZnO has high electron mobility, wide band gap and strong luminescence at room temperature. The photosensitivity of ZnO can be enhanced by the decrease of its dimensions down to nanostructures [1] and by its combination with graphene in hybrid structures. In such hybrid structures graphene can act as an excellent electron acceptor and transport material of photoinduced in ZnO electrons [2]. Graphene and ZnO have similar hexagonal crystal lattices. Therefore, graphene substrate during ZnO synthesis promotes epitaxial growth of ZnO that can promote formation of crystalline ZnO nanostructures. Both materials – ZnO and graphene - are not toxic, they are chemically stable and compatible with most organics, bio- and gas molecules. Therefore, combination of these materials in G/ZnO nanolaminates (“sandwich” type multilayer nanostructures) is perspective for applications in sensors and optoelectronic devices.

In this work 100 nm thin G/ZnO nanolaminates were fabricated by alternating ZnO deposition and graphene transfer. The deposited thickness of individual ZnO layers was from 10 to 100 nm, and number of graphene layers in nanolaminates was from 1 to 11. ZnO nanostructures were synthesized by atomic layer deposition (ALD) method. While graphene was synthesized using chemical vapour deposition (CVD) method and transferred on top of ZnO layers by polymer-based transfer technique. Structure and optical properties of fabricated G/ZnO nanolaminates were analysed using X-ray methods, TEM, AFM, Raman and optical spectroscopy. Obtained results were analyzed taking into account possible stain and charging effects of graphene in fabricated nanostructures.

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SOLVATES OF METHYL CHOLATE AND THEIR DESOLVATION

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Methyl cholate (MC; 3 α ,7 α ,12 α -trihydroxy-5 β -cholan-24-oic acid methyl ester) is white crystalline active pharmaceutical ingredient. It is insoluble in water, but soluble in medium polar organic solvents. It is used as dietary supplement as well as for treatment of inflammation and tumor. It is reported [1] that MC can form inclusion compounds with over fifty different organic substances. However, detailed information is provided only for some of the solvates: crystal structure information of methanol, ethanol, isopropanol, and acetonitrile has been published [2-4], and desolvation process and kinetics of acetonitrile solvate has been studied [5].

The aims of this study were to perform solvate screening and rationalize the driving force for the solvate formation as well as to rationalize the observed phase transformations and mechanism during the desolvation of MC solvates using structural and thermodynamic stability information.

In solvate screening it was determined that along with already known MC solvates with methanol, ethanol, isopropanol (Type 1 solvates), and acetonitrile (Type 2 solvate), numerous new solvates with nitromethane, dichloromethane (Type 2 solvates), toluene, *o*-xylene, 3-pentanone (Type 3 solvates), isopropyl acetate, 1,3-dioxolane, THF (Type 4 solvates), DMSO, DMF, water (Type 5 solvates), and isobutanol as well as three additional hydrates structurally similar to MC polymorphs or solvates can be obtained. Based on the similarities of the crystal structures and/or PXRD patterns as well as desolvation process, it was determined that MC forms five types of isostructural solvates (Type 1–5 solvates) as shown above. In the desolvation process also six new polymorphs of MC have been obtained.

Detailed analysis of the stability and desolvation mechanism of the obtained solvates was performed, by additionally exploring further phase transitions of the primary desolvation products under different conditions. It was observed that the primary desolvation product has crystal structure similar to that of the solvate, explaining the observation that desolvation of solvates produces multiple new polymorphs or even isostructural desolvates instead of thermodynamically more stable MC polymorphs I and II.

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CHEMOMETRICS FROM THE CALCIUM PHOSPHATES BY FOURIER TRANSFORM INFRARED SPECTROSCOPY

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Our study will investigate, how effective differentiation of Fourier transform infrared (FTIR) spectra can be done by FTIR processing techniques and chemometrics. FTIR spectroscopy is an important tool in the analysis of calcium phosphate. A major advantage of FTIR spectroscopy is, that spectra can be obtained from almost any physical state of sample (solutions, suspensions, powders). This research includes following steps of study:

- Sampling and Spectral recording.
- Pre-processing (normalization, baseline correction; “translation”) of spectra.
- Spectral processing with different software for analysis of spectra.
- Statistical analysis/Chemometrics (such as Principal component analysis (PCA), Factor analysis (FA), Pearson product-moment correlation coefficient (PPMCC) and Cluster analysis (CA). Cluster analysis uses Euclidean and Hierarchical methods).

In this research we found:

- Deconvolution of spectra improves understanding of materials that show complex FTIR spectra.
- PCA, CA proves to be valuable tool for analyses of FTIR spectra for research of testing methods and materials
- Modern software supports an efficient and intuitive analysis of sophisticated statistical analysis.

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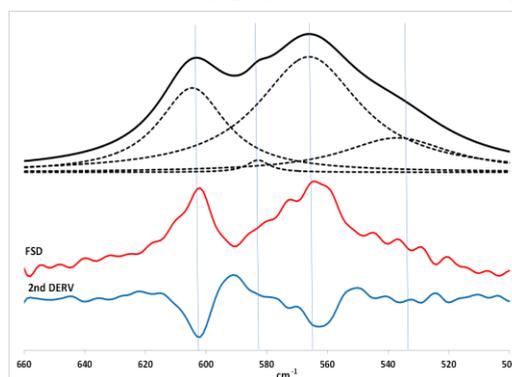


Fig. 1 A graph showing FTIR spectra curve fitting,

EVALUATION OF SOLID PHASE EXTRACTION AS A CLEAN-UP STEP FOR THE ANALYSIS OF DECHLORANE PLUS AND RELATED NORBORNENE-BASED FLAME RETARDANTS IN FOOD PRODUCTS

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Dechlorane Plus (DP) and dechlorane related compounds (DRCs) are halogenated flame retardants (FRs) widely applied for the past fifty years in polymer materials, coatings of electrical cables and wires, electronic components and textiles with the aim of reducing the possibility of fire [1]. Due to high bioaccumulation and biomagnification potentials, lipophilicity, persistence and long-range transport [2], DRCs are classified as persistent organic pollutants (POPs) and are suspected to access the food chains. As the low concentrations (up to pg g^{-1}) of the DRCs in food samples typically occurred [3], high analyte enrichment factor and extensive clean-up followed by the sensitive and accurate analytical measurement is required.

The main objective of this study was to optimize the efficiency of SPE clean-up step for 10 DRC representatives. Two different types of cartridges filled with neutral silica and Florisil (500 mg of sorbent per cartridge), as well as an affect of increasing of amount of silica sorbent in the cartridge (from 500 mg to 1000 mg) were evaluated. Seven elution systems were tested in terms of DRC elution efficiency.

Acetone and *n*-hexane/acetone mixture (90:10, v/v) were immediately excluded as possible eluents due to extremely low recoveries for Dec 603 and C110DP (up to 30 %). Excessively high absolute recovery values of brominated Dec 604 (from 110 to 140 %) were achieved for all investigated cartridges by applying of *n*-hexane, *n*-hexane / DCM (50:50, v/v), *n*-hexane / ethyl acetate (99:1, v/v) or toluene as elution solvents. Both silica and Florisil cartridges filled with 500 mg of sorbent with cyclohexane as eluent found to provide suitable recovery rates and could be recommended for purification of DRCs sample extracts. However, more detailed analysis of the results showed that the scatter of recovery rates for all analytes was higher for Florisil column (from 68 to 113 %) if compared to silica column (from 75 to 99 %) that determined the selection of Silica 500 mg / cyclohexane SPE combination as a clean-up step.

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IMPACT OF FERTILIZERS ON STABLE CARBON AND NITROGEN ISOTOPE RATIOS IN *LECCINUM AURANTIACUM**Lauma Buša¹, Kristīne Zadvinska¹, Arta Bārdule^{1,2}, Arturs Vīksna¹*¹*University of Latvia, Faculty of Chemistry, Jelgavas iela 1, Rīga, Latvia*²*Latvian State Forest Research Institute "Silva", Rīgas iela 111, Salaspils, Latvia
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Fungi can be named as some of the most vigorous agents for the decomposition of waste matter, and are an essential component of the soil food web [1]. They do have the ability to mineralize, release, and store various elements and accumulate toxic materials (such as pesticides, PCB's, dioxins etc.) [2] and thus act as bioremediators. One of possibilities to evaluate the uptake pattern of anthropological pollution in fungi is to use stable isotope ratio masspectrometry (SIRMS).

In the research *Leccinum Aurantiacum* samples from hybrid aspen experimental plot (lat: 56.6919, lon: 25.1370) were analysed. The plot was fertilized with biogas production residues or digestate (30 tonnes ha⁻¹), wastewater sludge (10 tonnes_{DM} ha⁻¹) and wood ash (6 tonnes_{DM} ha⁻¹) in the spring of 2011. The samples were collected in the years 2014 and 2015.

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 δ¹³C values are expressed relative to VPDB and the δ¹⁵N values relative to AIR.

*Table 1***Mean δ¹³C and δ¹⁵N values in *Leccinum Aurantiacum* samples from two years**

Fertilizer	Year	δ ¹³ C _{VPDB}	δ ¹⁵ N _{AIR}
Control	2014	-26.01 ± 0.02	8.50 ± 0.08
	2015	-26.7 ± 0.1	8.6 ± 0.4
Digestate	2014	-26.44 ± 0.05	10.96 ± 0.03
	2015	-26.86 ± 0.01	10.2 ± 0.2

The results show clear tendency that the δ¹⁵N values of *Leccinum Aurantiacum* from the soil fertilized with digestate are elevated, compared to the samples from soil with no additional fertilization. This agrees with previous researches that show enrichment in ¹⁵N values when nitrogen rich fertilizers are used [3]. In the research the effect of nitrogen rich fertilizer can be observed even four years after it has been used.

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ANALYTICAL CHEMISTRY APPLICATIONS IN TORMA (ESTONIA) AND HÖGBYTORP (SWEDEN) LANDFILL RESEARCH

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Landfills in common sense are considered as places where the life cycle of products ends [1]. The approach known as landfill mining (LFM) can deal with former dumpsites and is a step further in the waste management called “Beyond the zero waste”. Applied LFM projects in Sweden and Estonia have shown the potential of excavated waste as potential for recovery of lost material back into the economic cycle. [1,2]. Two landfills were chosen – Torma municipal landfill in Estonia and Högbytorp industrial landfill in Sweden. Waste was excavated, trommelled, screened and in this study fine fraction was analyzed regarding methods explained below. The aim of this study was to determine whether the fine fraction material express interest in future for recovery of major, minor and trace elements, including rare earth. Total amount of metals in fine fraction (FF) was performed by AAS and ICP-MS, easy extractable fractions were determined by modified sequential extraction procedures followed by spectrometry tools. Analytical research by using wet acid digestion for homogenised samples were followed by atomic absorption spectrometry (AAS) and inductively coupled plasma mass-spectrometry (ICP-MS) measurements to provide results on potentially recoverable metals in landfill waste from case studies of municipal and industrial dumps in Baltic adjacent countries (core and refractory: Ca, Al, Fe, Ba, Cu, Cr, Fe, K, Na, Mg, Mn, Pb, Zn, Co, Ni by AAS and Ba, Sr, Rb, As, Cs, Th, REEs as Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu by ICP-MS. Additionally easy extractable (mobile) fraction of metals was studied by the use of sequential extraction method. The extraction procedure included three steps: 1) Water-soluble fraction - deionised and heated (40 °C) water was used as extraction agent. 2) Acid-soluble fraction. 0.11 M CH₃COOH was added. 3) Reducible fraction. The residue from the 2nd step of fractionation was collected and poured into a 100 mL glass beaker. 20 mL of 0.5 M NH₂OH ×HCl was added. Concentrations of metalloids and metals, critical and REEs were detected by FAAS using *AAnalyst 200* (PerkinElmer) for major and some minor elements, but trace elements, rare earth and sequential extraction performed samples by ICP-MS (PerkinElmer ELAN DRC-e). Preliminary results on elemental concentration from Högbytorp and Torma landfills show wide range of macro and trace elements accumulated in fine fraction of waste. Most macro elements are Ca (20-53%), Fe (18-54%), Al (12%) and Mg (7-9%), followed by microelements that are in negligible or economically not feasible amount nowadays to provide for extraction. REEs if counted together are 25 mg/kg in Torma and around 50 mg/kg in Högbytorp, but statistical distribution shows that from all REEs Ce has 34-35%, La around 19%, Nd 18-20%, Yt 8-10%, Pr 4-5%, Sc 2-4%, Sm and Gd around 3%. Screening results acquired during the studies on sequential extraction procedure show that water and weak acid extraction provide negligible amount of critical elements and REEs, with very few exceptions, however few elements are easy extractable and might have economic interest for resources recovery. Research in Torma and Högbytorp provided results on fine fraction in

landfill waste containing potentially recoverable metallic, critical and REE resources. Although REEs are in significantly lower concentration than in primary ores and secondary resources - Fe, Al, Cu, Pb, Ni and some other might be of interest for extraction in future. REE deposits can be referred as “reserves or bank account”.

Acknowledgement:

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DETERMINATION OF POLLUTION IN HAZARDOUS TOXIC WASTE DUMP IN OLAINĒ REGION

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Hazardous toxic waste dump in Olaine region historically has been one of the most polluted areas in Latvia. Total area of the landfill takes up to 130 000 m². And its contamination has a significant impact on the environment causing serious threats of pollution. The area has been closed for several years, but the treatment works only ended in October 2015. Despite the fact that the landfill territory was under a series of several treatment works, the spreading of contamination has not yet been stopped. Considering that the landfill is not so far away from agricultural and residential territories (the nearest house is located approximately 600 m away from the landfill), it is important to evaluate the pollution not only in the landfill itself but also in its surrounding territories.

This work contains analysis of surface water and soil samples. Determination of chemical oxygen demand (COD), iron, nitrogen and chloride ions in surface water samples and determination of zinc, nickel and lead content in soil samples was realized. Experimentally spectrophotometric, atomic absorption spectroscopic, ionometric and titrimetric methods were used. This work includes evaluation of surface water pollutant concentration changes according to seasonal changes.

The results of this work shows that surface waters are contaminated with organic pollutants. Such conclusion is made on the basis of the results of the chemical oxygen demand (COD) analysis. For clear surface waters the value of COD varies between 8 to 12 mg per litre, but results obtained in these experiments show values from 5 to 34 mg per litre. These results also show the relationship between the sampling distance from the landfill and the sample degree of purity. Also the inorganic nutrient concentration of some analysed surface water sample exceeds maximum permissible limits.

KINETIC METHOD FOR STUDYING THE ANTIRADICAL ACTIVITY OF PLANT EXTRACTS

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Lipid autooxidation represents a serious problem, which relates to the formation of free radicals involved in the ageing processes of tissues and pathologies such as cancer or cardiovascular diseases [1]. Therefore, it is necessary to protect human tissues from free radicals by endogenous and exogenous antioxidants from a natural or synthetic origin.

Nowadays, preference is given to the natural antioxidants, such as plants and vegetables. In this study the kinetics of antiradical activity of the certain plant species is investigated. *Centaurium erythraea* Rafn, *Linaria loeselii* Schweigg and *Dracocephalum ruyschiana* L. are plant species that contain a wide variety of biologically active compounds (amino acids, polyphenolic compounds, flavonoids etc.). The phytochemical composition of the studied plants reveals their probable anti-ageing, anti-UV and bleaching influence on human skin which is of a great interest in the field of cosmetology.

The antiradical activity of investigated plant ethanolic extracts was studied using UV/VIS spectroscopy; the phytochemical composition of the plants was investigated by HPLC/MS; Runge – Kutta method was applied to obtain kinetic models characterising antiradical activity of the studied plants and determining kinetic parameters of the process.

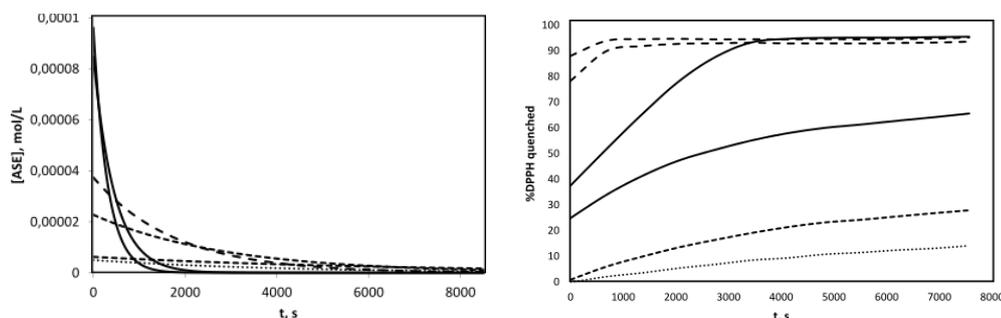


Fig.1. Kinetic curves for antiradical activity of *Centaurium erythraea* Rafn, *Linaria loeselii* Schweigg and *Dracocephalum ruyschiana* L.

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ALTERATION OF ELEMENTAL COMPOSITION AND MINERAL CONTENT DEPENDING ON PLANT BIOMASS TYPE AND ITS PROCESSING METHODS

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The demand for renewable resources is growing and one of the most perspective resources is biomass because it regenerates in a short period of time. The research of biomass refining to biopellets or to a different sort of biofuel has become more important. Plant biomass is an organic substance which is available everywhere and it grows back in a short period of time comparing it to fossil fuels. Plant biomass includes wood, grain, corn, agricultural and forestry residues and all kind of water plants.

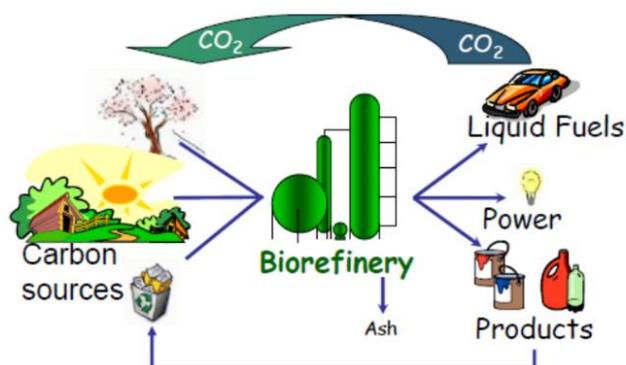


Fig. 1 The principal of biorefining [1].

This work evaluates alteration of elemental and mineral composition of biomass samples treated with ultrasound-assisted extraction and torrefaction. Total number of samples evaluated was 70, elemental composition was determined to 67 of them and mineral content was determined to 11 of them. Different methods of determination of mineral content include FES, FAAS, WD-XRF and ICP-MS were used, while elemental composition was determined with elemental analyzer. In the current study, different correlations between untreated and treated biomass samples were evaluated and the effect of elemental composition and mineral content on heating values was calculated.

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DETERMINATION OF PATULIN IN LATVIAN ORIGIN JUICES, JAMS AND SYRUPS EMPLOYING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY - MASS SPECTROMETRY

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Patulin is a polyketide lactone and toxic secondary metabolite produced by certain fungal species, e.g. *Penicillium*, *Aspergillus* and *Byssoschemys* [1] [2]. However, the greatest producer is *Penicillium expansum*, which is responsible for fruit decomposition, especially in apple and apple containing products [3]. Patulin, among different mycotoxins, occasionally was found as a contaminant in fruits, such as pears, apricots, peach also in vegetables, cereals and its by-products. This mycotoxin produced under certain conditions – high temperature, present of oxygen and low pH. Patulin is thermostable, so it's necessary to select undamaged fruit and strictly follow every step of production, especially in case of fruits, because of the high possibility of patulin as a natural contaminant [4].

A several analytical methods for patulin detection have been employed, including thin layer chromatography (TLC), gas chromatography - mass spectrometry (GC-MS), liquid chromatography - mass spectrometry coupled to ultraviolet (UV) [5] or diode array detector (DAD) [6] and high performance liquid chromatography - mass spectrometry which is the most suitable method in mycotoxin analysis providing better sensitivity [7].

AOAC 995.10 is an official method of determination of patulin in apple juice, which is the most common procedure with liquid-liquid extraction and purification with NaHCO₃ [8] [12]. However, there are several disadvantages specific to this methodology including use of large amounts of harmful solvent, such as ethyl acetate, besides this approach is time consuming. Those are few of reasons why the method is needed with more harmless solvents, several cleaning steps for reducing of the matrix effect and eliminating co-analytes and less time for preparing samples [5].

Final sample solution in our study was analyzed under the following conditions: the analytical column *Phenomenex C18* (50 x 3 mm, 1,7µm); mobile phases A: 5mM ammonium formate in water B: acetonitrile with flow rate 0,4 mL/min. Patulin analyses were performed by UHPLC-MS/MS (SCIEX Qtrap 5500) with electrospray ionization operated in MRM.

This method was applied for determination of patulin in 64 different juice, jams and syrups to compare and investigate the contamination of this mycotoxin in Latvian homemade products. Only 7 of 64 analyzed samples showed contamination of patulin in range from 5 to 45 ng/g which are below the level of limit set by European Union with Commission Regulation No. 1881/2006.

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**TECHNICAL LIGNIN EXTRACTION USING DIFFERENT IMIDAZOLIUM
TOSYLATE IONIC LIQUIDS**

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Chemical heterogeneity of technical lignin, conditioned by significant variations in lignin phenyl propane units (PhPU) structure, types of inter units links and presence of impurities (e.g. carbohydrates) hinders their applications as a high value added products, e.g. as antioxidants, antimicrobial agents etc. Ionic liquids (ILs), recognized as "green" solvents, became very popular for fractionation, dissolution and purification of biomass components. Purification of technical lignins opens new opportunity for their application in different area, from production of polymer composite materials to cosmetic and health care commodity [1]. In the present study, technical lignin was treated using different imidazolium tosylate based ILs differed by cations: 1-butyl-3-methylimidazolium tosylate [C4mim]oTs **1**, 1-octyl-3-methylimidazolium tosylate [C8mim]oTs **2** and 1-dodecyl-3-methylimidazolium tosylate [C12mim]oTs **3** (shown in Fig.1.). The aim was to obtain lignins of high purity for further application as antioxidants.

The composition and structure of the untreated and treated with ILs lignins were studied using analytical pyrolysis (Py-GC/MS/FID) and NMR methods. Antioxidant activity of the lignin samples obtained was assessed using two test (DPPH[•], ABTS^{•+}) methods.

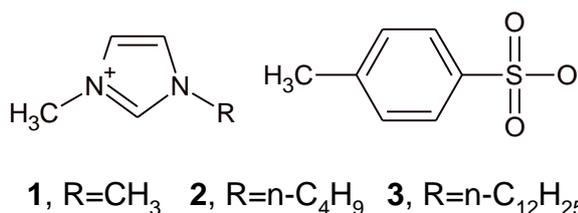


Figure 1. Imidazolium tosylate based ILs differed by cations

It was shown, that the purity of the lignin significantly increases as the result of the treatment with ILs. Structure of obtained lignin depends on used IL and its treatment conditions and antioxidant activity increase comparing with parent lignin.

It can be concluded, that ILs are suitable solvents for the selective isolation of the purified lignin component from technical lignins.

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PRODUCTION OF GRADUALLY VARIABLE THICKNESS POROUS ALUMINA THIN FILMS

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Anodic aluminum oxide (AAO) has many applications ranging from corrosion protective coatings to templated nanostructure synthesis [1]. Precise control of AAO thickness in optical subwavelength range enables design of multilayer systems with useful properties for interferometric sensors, filters and other devices. Particularly interesting are multilayer or sandwich structures containing noble metals, which support plasmonic modes [2]. However, accurate thickness control during ultra-thin AAO synthesis is difficult, since growth rate among others is influenced by current density distribution, domain structure of aluminum substrate and electrochemical reaction must be interrupted before or shortly after stable pore growth regime is established.

In order to obtain regions of desired thickness, we have developed a method of AAO growth with designed thickness gradient, which is achieved by mechanical motion of aluminum plate during anodization process. For instance change from 50 to 300 nm AAO thickness within 1 cm distance can be achieved. The thickness is determined by scanning electron microscopy analysis of AAO film cross-section or non-destructively by measurement of optical reflection spectra, which is fitted to mathematical model using matching and propagation matrices. An automated optical thickness mapping was developed in order to find regions with desired properties.

Preliminary results show AAO thickness dependent coupling to plasmonic modes in metal-AAO metal structures and fluorescence enhancement from materials trapped between the two metal layers.

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CHARACTERISATION OF POLYPHENOLS IN DIFFERENT VARIETIES OF *SALIX* BARK

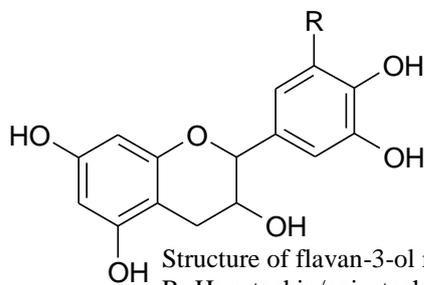
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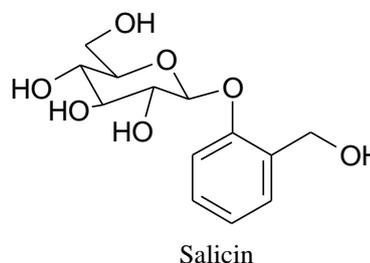
Willow bark extracts can be found as an ingredient in cosmetics and personal care products due to its astringent, anti-inflammatory, and soothing properties. Chemical composition of willow bark extracts mostly associated with high salicylate-like phenolic glycosides and condensed tannin content, but polyphenol profiles vary among species [1]. The purpose of the present study was to investigate characteristics of the extracts from willow bark collected from different *Salix* species growing on plantation in Latvia and examine the polyphenol chemical profile. The samples of willow bark were collected in Skrīveri region, Latvia from willow plantation on agricultural land. Trees were approximately three years old, samples were collected in November. Extracts were obtained using accelerated solvent extraction with ethanol water mixture (70:30 v/v) after lipophilic extractive removal. Analysis of extracts was performed on liquid chromatography – masspectometry using C18 column. Total phenolic was determined using Folin-Chicoulteu method.



Structure of flavan-3-ol monomer

R=H: catechin/epicatechin (procyanidin)

R=OH: gallocatechin/ epigallocatechin (prodelphinidins)



Salicin

It is significant differences in chemical composition and antioxidant activity between extracts obtained from various *Salix* species, it brings to possible multi valuable product productions. Comparing total phenolic content with extraction yield, there is no correlation. There is no significant differences between phenolic content in Tora, Klara, Stina and Inger (~ 0.4 GSE g •g extract⁻¹), more phenolic is in Lisa and Sven, but the lowest in Gudrun extracts 0.3 GSE g •g extract⁻¹. In conclusion, further studies will be needed to characterize the individual phenolic compounds, quantify them and found practical application.

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DETERMINATION OF SUGARS AND THEIR DERIVATIVES IN PYROLYSIS CONDENSATES WITH LC-MS

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Biomass based polysaccharides are a potential renewable source of monosaccharides, therefore the development and optimization of methods for the analysis of sugars and their derivatives are always interesting. Investigations about the content of sugar derived compounds in the products of thermochemical processing of wood are important in order to develop optimal technologies for producing certain sugars, as well as to understand the mechanisms of the destruction of wood. Our research focuses on the determination of sugars and their derivatives in the products of wood pyrolysis.

At certain conditions the wood pyrolysis process gives a 75 % yield of condensable products. This condensate consists of more than a hundred individual compounds belonging to various chemical classes, so it is challenging to develop a comprehensive methodology for analyzing pyrolysis condensates. One of the most often encountered and also valuable compounds are sugar derivatives produced as a result of the pyrolysis of wood polysaccharides – cellulose and hemicelluloses. Wood origin sugars can be used to produce biobased chemicals or bioethanol in order to move from fossil to renewable resources [1].

The most popular sugar determination method is high performance liquid chromatography – most often with refraction index or evaporative light scattering detectors [2]. However, with the development of mass spectrometry technologies, it has become possible to perform sugar and sugar derivative identification and quantitation with mass spectrometry. Still there are several difficulties with sugar determination (isomer separation, poor ionization, contamination of the mass spectrometer), especially, in case of such complicated matrix as pyrolysis condensates.

The study was implemented within the National Research Programme “Forest and earth entrails resources: research and sustainable utilization – new products and technologies” (ResProd) Project Nr.3 “Biomaterials and products from forest resources with versatile applicability”.

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HYDROTHERMAL PROCESSING OF DIFFERENT CALCIUM PHOSPHATES BY H₂O₂ AND THEIR INVESTIGATION BY LIGHT STABLE ISOTOPE RATIO MASS SPECTROMETRY

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Calcium phosphates as biomaterials are used already for several decades. Of particular importance and more essential is a wide range of clinical applications - both for coating of metallic implants and in bone grafts for bone regeneration. Among all the calcium orthophosphate representatives' hydroxyapatite (HAp) and tricalcium phosphates (TCP) are the most promising biomaterials. Nevertheless mammals bone is a very complicated hierarchical material, though chemically synthesized biomaterials represent almost excellent chemical similarity to inorganic phase of biological apatites [1]. Although synthetic HAp and TCP has some shortcomings as weak antibacterial property - the undesirable infection threats could be minimize by improving properties of the above mentioned biomaterials [2]. One of the widely used approaches for properties' improvement is incorporation of different ions, since the apatite lattice is very tolerant of substitutions. Hydrogen peroxide is commonly used as effective disinfectant and it is also found in the human body – it is generated by phagocytes to modulate the inflammatory processes, but high concentrations for internal use can damage cells which are involved in bone replacement. Low peroxy ion concentration and slow release could provide additional antibacterial activity of synthesized biomaterials.

The current research focused on the peroxide ion incorporation in calcium phosphates. Different materials - strontium hydroxyapatite (SrHAp), hydroxyapatite (HAp), tricalcium phosphate (TCP) and calcium phosphate were exposed 50% wt. H₂O₂ in a closed hydrothermal steel vessel system under mild conditions at 150 °C. The content of hydrogen peroxide was determined by permanganometry and continuous flow isotope ratio mass spectrometry was used to determine δ¹⁸O values for treated with H₂O₂ and untreated calcium phosphates.

Sample	ω(H ₂ O ₂), %	δ ¹⁸ O, ‰	S _n , ‰
75%-SrCaHAp	-	15.43	0.19
75%-SrCaPerAp	2.01	16.52	0.16
HAp	-	13.2	0.3
HPerAp	1.30	16.7	0.1
Ca ₃ (PO ₄) ₂ untreated	-	16.90	0.40
Ca ₃ (PO ₄) ₂ treated	0.92	19.86	0.02
TCP untreated	-	19.2	0.2
TCP treated	0.50	20.2	0.2

Table 1. ωH₂O₂ and δ¹⁸O values of treated with H₂O₂ and untreated apatite materials.

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SIMULTANEOUS SCREENING AND QUANTIFICATION OF AMINOGLYCOSIDE RESIDUES IN HONEY BY MIXED-MODE HYDROPHILIC INTERACTION LIQUID CHROMATOGRAPHY COUPLED TO TIME-OF-FLIGHT MASS SPECTROMETRY WITH HIGH-TEMPERATURE ELECTROSPRAY IONIZATION

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Aminoglycoside class antibiotics are used in apiculture and agriculture particularly for treatment of bacterial infections such as American and European foulbrood disease and fire blight of pome fruits. Therefore, traces of aminoglycoside antibiotics could be present in honey and honey-based products [1,2].

A highly selective method based on mixed-mode liquid chromatography coupled to time-of-flight mass spectrometry with high-temperature electrospray ionization has been developed for simultaneous determination of 6 aminoglycoside antibiotics – dihydrostreptomycin, gentamycin C1, kanamycin A, neomycin, streptomycin and spectinomycin.

The analytes were extracted with 1% trichloroacetic acid solution followed by solid-phase extraction (SPE) cleanup using 200 mg Strata-X PRP (*Phenomenex*) cartridges. The influence of pH on the SPE procedure was studied. The best recoveries were obtained at pH 9 followed by acidic elution using water:acetonitrile:formic acid 94:5:1 (v/v/v) containing 10 mM of ammonium formate showing that deprotonation of the target compounds is fundamental in order to ensure the maximum retention on the SPE column.

The chromatography separation was performed on a SIELC Obelisc R (2.1 × 150 mm, 5 μm) column by gradually decreasing the pH value of the mobile phase whilst increasing its overall polarity using triple mobile phase system of water (A), acetonitrile (B) and water with 1% formic acid (C) at a flow rate of 0.5 mL·min⁻¹. This allowed a successful separation of all six compounds without the use of derivatization agents and mobile phase additives commonly employed in liquid chromatography based methods for determination of aminoglycoside antibiotics.

A time-of-flight mass spectrometer equipped with a high-temperature electrospray ionization source IonBooster™ (IB) was operated in MS/ddMS² mode thus allowing simultaneous acquisition of full MS scan and data-dependent MS² scan for scheduled precursor list of target compounds. This technique is generally used in proteomics and metabolomics for investigation of unknown compounds, but can be modified to be fit for the purpose of screening and quantification applications. The optimization of IB parameters led to higher ionization efficiencies in comparison to conventional ESI source and showed complete elimination of [M+Na]⁺ and [M+NH₄]⁺ adducts along with reduced formation of doubly charged ions.

The method was validated according to the guidelines laid down by European Commission Decision 2002/657/EC and applied for the determination of aminoglycoside

antibiotics in Georgian honey. 5 out of 49 analyzed samples showed contamination levels above the limit of quantification with maximum concentration of $114 \text{ ng} \cdot \text{g}^{-1}$ for streptomycin.

This research was financially supported by the Project No. NFI/R/2014/010 "Establishing of the scientific capacity for the management of pharmaceutical products residues in the environment of Latvia and Norway"

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COUPLED THERMOGRAVIMETRIC ANALYSIS/INFRARED SPECTROSCOPY FOR INVESTIGATION OF PROPERTIES OF POLYMER-IONIC LIQUID COMPOSITE MEMBRANES

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For more than a decade sulphonated poly(etheretherketone) (SPEEK) have been considered a promising material for proton electrode membrane fuel cells (PEM FC) due to its low cost and good proton conductivity. However, for SPEEK to possess sufficient proton conductivity it needs to be hydrated. This significantly lowers the temperature range at which SPEEK PEM can be deployed, thus increasing overall cost of PEM FC since more effective catalyst and fuel of higher purity is needed. Additionally, high water content has a negative impact on structural integrity of PEM [1]. These factors have led to search for functional replacements of water in SPEEK. Various procedures have been proposed, such as addition of ionic liquids (ILs) [2], zirconium oxide [3], or crosslinking [4]. ILs are interesting in particular due to possibility of combination of various cations and anions, creating an IL suitable for specific situation. Incorporation of ILs in composite SPEEK membranes results in improvement of the proton conductivity but also in degradation of mechanical properties [5]. Due to wide range of decomposition temperature of ILs, an insight in the behaviour of SPEEK-IL composite membranes at higher temperatures might be valuable.

In this work, decomposition temperatures of all compounds of composite membranes were determined, as well as decomposition products identified. It was determined that decomposition temperature among ILs differs significantly less when ILs are incorporated in SPEEK polymer membrane, indicating an interaction between ILs and the polymer matrix. It was also noted that increasing IL content in membrane desulphonation temperature increases as well, regardless of the structure of individual ILs. A possibility of determining the degree of sulphonation (number of sulphonic groups per monomer) of SPEEK from combined thermogravimetric analysis/infrared spectroscopy data was recognized.

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PURIFICATION OF ILLITE CLAY MINERALS

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Clays are the most common sedimentary rocks, they are easily available and have low cost. In Latvia, clays are mainly used for different kinds of building ceramics production. However, because of clay mineral particle nanometer size, high cation exchange capacity (CEC) and swellability, perspective is to use clay minerals for synthesis of polymer nanocomposite materials [1]. Unfortunately, clay minerals often are found mixed or associated with other coarse – grained minerals, such as quartz, carbonates and feldspar. Therefore, clay minerals must be purified.

In Latvia, illite containing clays are the most frequent. Therefore, purification study focused on them. Clay mineral fraction separation method [2] was used for Kuprava and Liepa deposit clays. This method is based on dispersing illite clays in sodium tripolyphosphate solution, coarse – grained particles sedimentation and clay – size fraction coagulation with acetone and hydrazine dihydrochloride reaction product.

The proposed method allows to get rid of calcite, dolomite minerals impurities and significantly reduce the quartz content in the clay samples. Major crystalline phases of clay – size fraction is illite, mixed layered illite – smectite and kaolinite, with smaller quantities of quartz. The CEC of the clay samples determined by methylene blue method increased from 13 meq/ 100g for raw illite clay to 28 meq/ 100g for the illite clay-size fraction. Separated clay – size fraction quantity strongly depends on clay dispersing techniques. The most efficient dispersion of clay particles in sodium tripolyphosphate solution were obtained if the clay samples were left to swell for 24 hours, and then treated in an ultrasonic bath.

It should be noted that 1.5 % of coagulant are strongly adsorbed on the clay particle surface. Coagulant can be removed chemically by oxidization with hydrogen peroxide. After oxidation CEC of clay samples increases to 38 meq/ 100g.

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CHARACTERISATION OF MODIFIED LITHIUM ORTHOSILICATE PEBBLES WITH NOBLE METAL IMPURETIES

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Modified lithium orthosilicate (Li_4SiO_4) pebbles with additions of titanium dioxide (TiO_2) are suggested alternative solid breeder material for the tritium breeding in deuterium-tritium (D-T) nuclear fusion reactors [1]. The noble metals – platinum (Pt), gold (Au) and rhodium (Rh), can be introduced into the modified Li_4SiO_4 pebbles during the melt-based process, due to the corrosion of Pt-Rh and Pt-Au alloy crucible components. In this study, the surface microstructure, chemical and phase composition of the pebbles with different contents of the noble metals was analysed.

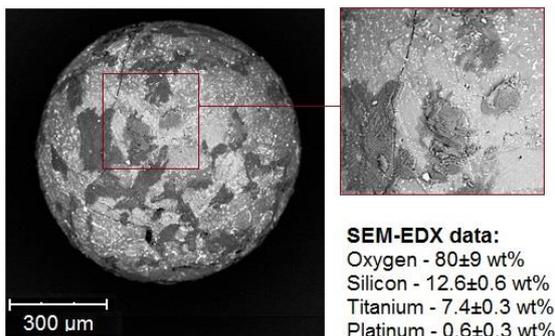


Fig. 1. The surface microstructure and chemical composition of the modified Li_4SiO_4 pebbles with noble metal micro-impurities

Using scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) spectroscopy, mainly oxygen, silicon, titanium and Pt trace-impurities were detected on the pebble surface (Fig. 1.). The Pt trace-impurities are heterogeneously distributed and localise mainly on grain boundaries or as inclusions. In the powder X-ray diffractometry (p-XRD) patterns, the peaks of Li_4SiO_4 and lithium metatitanate (Li_2TiO_3) have been detected. The peaks of the corrosion products – metallic Pt or lithium platinate (Li_2PtO_3), were not detected, most likely due to very small amounts or the overlapping of the peaks with the other phases.

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EFFICIENCY AND PRACTICAL APPLICATION OF SOLVATIC SORPTION MODEL FOR HPLC METHOD DEVELOPMENT AND OPTIMIZATION

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It is no secret that the development and optimization of HPLC gradient methods can be time consuming and require many experiments [1,2]. However, scientists can no longer afford to use the ‘trial-and-error’ approaches previously often applied. In such areas as the pharmaceutical and clinical industries as well as food and beverages it is necessary to develop rapid optimization methods. So analysis time and financial considerations are also used as optimization criteria [3]. Consequently, nowadays, one of the most significant problems in chromatography is the prediction opportunity of compound retention times and chromatographic conditions.

The aim of this work is to study the efficiency and practical application of the solvatic sorption model for method development and optimization for highly polar and charged analytes, when working with human biological materials, such as blood serum, plasma, and urine. One of the highly polar and charged analytes in human biological materials is amino acids. Inborn errors of amino acid metabolism are a result of the accumulation of toxic metabolic products in the body system or the inefficient breakdown of amino acids. Several inborn errors of metabolism cause changes in the biological materials’ quantitative and qualitative compositions. So, the practical efficiency of the solvatic sorption model was verified by the development and optimization of a method for the detection of phenylisothiocyanate derivatives of amino acids in human biological materials.

Summarizing the obtained results, it can be argued that the developed and optimized method for the detection of phenylisothiocyanate derivatives of amino acids in human biological materials is useful for the selective screening of different inherited metabolic disorders. That confirms that the model is highly effective for highly polar and charged analytes.

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