83rd International Scientific
Conference of the
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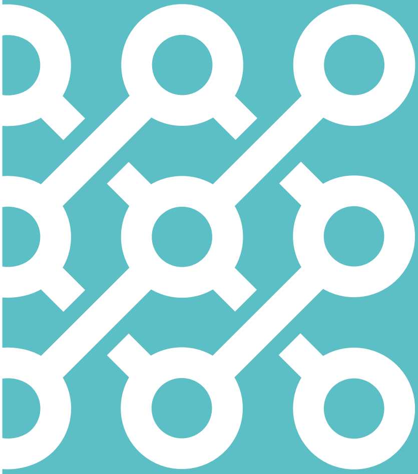
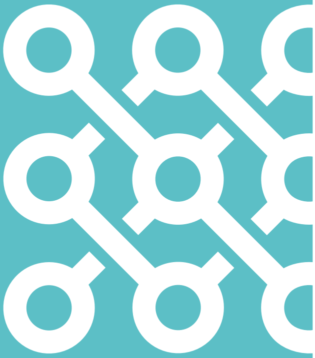
# CHEMISTRY SECTION AND SECTION OF INSTITUTE OF CHEMICAL PHYSICS

## Book of Abstracts





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# CONTENT

SECTION OFANALYTICAL AND PHYSICAL CHEMISTRY

## SECTION OFORGANIC CHEMISTRY

## SECTION OF INSTITUTE OF CHEMICAL PHYSICS

# SECTION OF ANALYTICAL AND PHYSICAL CHEMISTRY

# ICP-MS ANALYZER CALIBRATION STRATEGY

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Due to the need to determine small mass concentrations of $Cs^+$ and $Co^{2+}$, etc. elements in aqueous solutions, which are limited by the capabilities of the ICP-MS device, special strategies must be developed to achieve these goals. If the calibration is linear and the measurement data are homoscedastic, data processing is described in detail in the educational literature [1, 2]. In other cases, it is necessary to create formulas for calculating both the calibration equation constants and their standard deviations, as well as the standard deviation of the analysis results. Considering that the data obtained in measurements with the ICP-MS device are strongly heteroscedastic, and the standard deviations of the measurements with a high correlation coefficient are linearly related to the mass concentration (or analytical signal) (Figure 1), it is necessary to take this into special account in data processing. Table 1, 2 summarizes the results of determining the analysis results and their standard deviations for several approaches. The calibration graph includes 7 measurements, the analytical signal I of the analysed sample is measured once, but in the case of heteroscedastic data, the standard deviation of the measurements of the zero-mass concentration solution is not considered.

It can be seen that the precision and accuracy of the analysis results is significantly improved if a nonlinear, in this case, parabolic calibration graph is chosen. Of course, the choice between a linear and a nonlinear calibration graph must be made by assessing the level of significance of the constants of the calibration equation.

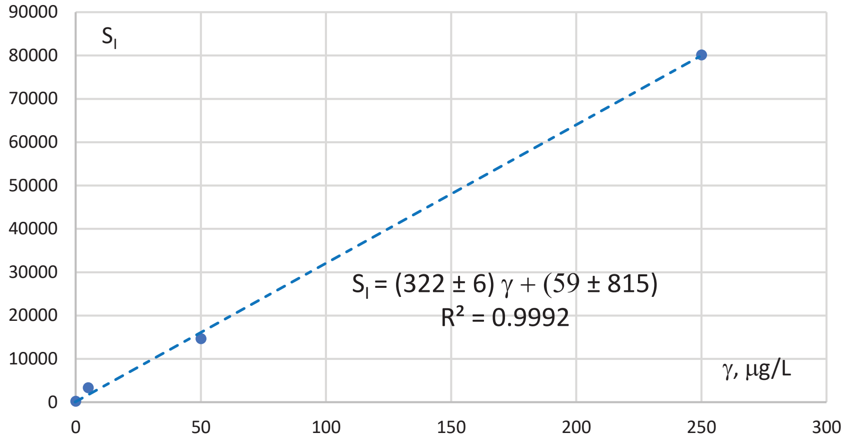

*Figure 1.* Dependence of the signal standard deviation on $Cs^+$ concentration

Assuming the homoscedasticity of the data in the case of parabolic calibration $\alpha_a = 8.4 \cdot 10^{-6} < 0.1$ confirms the statistical significance of the coefficient of the quadratic term. However, considering the heteroscedasticity of the data, the coefficient *a* becomes statistically insignificant ($\alpha_a = 0.84$), and the statistical significance of the coefficient c also decreases. This indicates that the heteroscedasticity of the data plays a dominant role in the assessment of the analysis results and their standard deviations.

*Table 1.* $Sr^{2+}$ mass concentrations (μg/L) and standard deviations assuming homoscedastic data

| | **Linear homoscedastic** | | **Parabolic homoscedastic** | |
|---|---|---|---|---|
| **I, Mc/s** | **c ≠ 0** | **c = 0** | **c ≠ 0** | **c = 0** |
| 1.0 | 73.4 ± 0.3 | 73.4 ± 0.3 | 73.07 ± 0.03 | 73.10 ± 0.09 |
| 0.5 | 36.6 ± 0.3 | 36.7 ± 0.3 | 36.20 ± 0.03 | 36.21 ± 0.04 |
| 0.2 | 14.6 ± 0.3 | 14.7 ± 0.3 | 14.40 ± 0.02 | 14.41 ± 0.03 |
| 0.1 | 7.3 ± 0.3 | 7.3 ± 0.3 | 7.20 ± 0.02 | 7.19 ± 0.03 |
| 0.05 | 3.6 ± 0.3 | 3.7 ± 0.3 | 3.61 ± 0.02 | 3.59 ± 0.02 |
| 0.01 | 0.7 ± 0.3 | 0.4 ± 0.3 | 0.73 ± 0.02 | 0.72 ± 0.02 |
| Significance levels α | $\alpha_c = 0.52$<br>$R^2 = 0.99997$ | | $\alpha_a = 8.4 \cdot 10^{-6}$<br>$\alpha_c = 0.16$<br>$R^2 = 0.9999998$ | |

*Table 2.* $Sr^{2+}$mass concentration (μg/L) and standard deviation determination options for heteroscedastic data

| | **Linear heteroscedastic** | | **Parabolic heteroscedastic** | |
|---|---|---|---|---|
| **I, Mc/s** | **c ≠ 0** | **c = 0** | **c ≠ 0** | **c = 0** |
| 1.0 | 73.3 ± 1.2 | 73.3 ± 1.0 | 72.2 ± 1.4 | 73.2 ± 1.3 |
| 0.5 | 36.7 ± 0.6 | 36.7 ± 0.5 | 36.7 ± 0.7 | 36.6 ± 0.6 |
| 0.2 | 14.7 ± 0.2 | 14.7 ± 0.2 | 14.7 ± 0.3 | 14.7 ± 0.2 |
| 0.1 | 7.33 ± 0.12 | 7.33 ± 0.11 | 7.34 ± 0.14 | 7.34 ± 0.12 |
| 0.05 | 3.67 ± 0.06 | 3.67 ± 0.05 | 3.67 ± 0.07 | 3.67 ± 0.06 |
| 0.01 | 0.733 ± 0.011 | 0.733 ± 0.010 | 0.734 ± 0.014 | 0.734 ± 0.012 |
| Significance levels α | $\alpha_c = 0,92$ | | $\alpha_a = 0.84$<br>$\alpha_c = 0.87$ | |

Considering the heteroscedasticity of the data, the accuracy of the analysis results improves in the area of the lowest concentrations.

**Acknowledgements.** The research was funded by the European Defence Fund project “First research action for Medical counter measures performed in the frame of the RESILIENCE FPA consortium (RESILIENCE-R-2023), project No. 101168024.

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# CHEMICAL COMPOSITION OF METALLIC ALLOY AND POLYMER PENCILS

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Pencil cores typically consist of graphite, clay, and binders such as wax, resin, or polymer. The selection and proportion of clay and binders vary across manufacturers, resulting in distinct chemical compositions and characteristics unique to each brand or even specific batch [1].

The presence of chemical elements and inorganic impurities directly influences the characteristics of pencil cores, making this information important for quality control and analytical research. In forensic investigations, chemical analysis of pencil marks can serve as a valuable tool for determining whether a particular entry is genuine or has been altered. Since pencil-written text is easily erased, an element-based analysis can provide crucial insights, such as verifying if a specific entry was made with the same pencil or establishing the order in which markings were created [1, 2].

The aim of this research is to investigate chemical composition of metallic alloy and polymer pencils from different manufacturers.

Pencil core samples were mineralized using closed microwave digestion system with the mixture of $HNO_3$:HCl:$H_2O_2$ (6:2:4, V/V), and the element concentration were measured by ICP-MS. Both the pencil marks on paper and a piece of the pencil core were analysed using SEM-EDX.

The results revealed that metallic alloy pencils predominantly contain Si, Al, S, Fe, Ca, K, Mg, and Cu. The high content of Si and Al suggests the use of kaolin clay in their production. One metallic alloy pencil was found to contain only graphite, raising concerns about inaccurate labelling.

In polymer pencils, significant differences were noted between brands. The “rOtring” polymer pencils contained high levels of Si, Al, Fe, Mg, and K, while “Faber-Castell” pencils contained higher content of Cl and P. Flexible polymer pencils contained a high content of Cl, indicating the presence of synthetic rubber (neoprene). The blue-coloured pencil cores contained higher levels of Ti, Si, Mg, Ca, Al and Cu due to added pigments such as $TiO_2$.

The chemical composition of pencil cores varies significantly based on manufacturer and depending on the types of clay and additives used.

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# HYDROTHERMAL HUMIFICATION OF SPRUCE GREENERY AS A TOOL FOR SUSTAINABLE PRODUCTION OF SYNTHETIC HUMIC SUBSTANCES

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Peat is the primary raw material for soil enhancers, but it is a slowly renewable fossil resource, and its extraction generates significant greenhouse gas emissions (mainly $CO_2$ and $CH_4$). According to the Latvian State Forest Research Institute "Silava", 70% of these emissions come from peat used in agriculture, with total emissions reaching 1709 kt $CO_2$ equivalent [1].

A sustainable alternative could be spruce greenery – a forestry by-product left behind after log extraction. This unused biomass, which can make up 50% of a spruce tree's dry mass, can be processed to extract valuable compounds. The remaining material, rich in lignin, cellulose, and hemicellulose, can then be converted into synthetic humic substances using hydrothermal humification process.

This study aims to promote end-of-waste approach in valorising low value forestry by-products by applying a novel hydrothermal humification process to produce synthetic humic substances that mimic the nature of natural peat humic substances, that could be used in agriculture. This waste conversion method produces significantly lower amounts of GHGs than peat extraction process and the main cornerstone of this method is that the biomass does not have to be energy-intensively dried prior to synthesis. The results of this research will contribute to developing high-value bioproducts from forestry residues, supporting circular economy principles in Latvia's bioeconomy.

Results show that the spruce greenery biomass can be successfully converted into synthetic humic substances. This study explores the optimal conditions for hydrothermal humification process such as catalyst concentration, duration of synthesis and the temperature of process to obtain the highest yield of both synthetic humic acids, fulvic acids and their low-molecular byproducts. Synthetic humic substances and their structural formation dynamics were analysed using contemporary analytical methods, such as FTIR, $^{13}C$-CPMAS-NMR and EPR spectroscopy. The formation dynamics of fulvic acids and by-products were investigated using spectrophotometric methods. This research provides fundamental knowledge of hydrothermal humification dynamics in use for production of synthetic humic substances.

**Acknowledgements**. This research was funded by the Rural Support Service Republic of Latvia project "Full-cycle processing of green biomass from skewers to produce high-value feedstocks for the chemical and pharmaceutical industries" (No. 23-00-A01612-000007).

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# BINDER-FREE CARBON AEROGEL ELECTRODES: ADVANCING SUPERCAPACITOR PERFORMANCE

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Carbon aerogel is one of the ideal materials for supercapacitors because of its high specific surface area and high conductivity [1]. Commonly, carbon aerogel-based electrodes are prepared using a polymer binder, which worsens the performance of the aerogel by blocking pores and decreasing electrical conductivity [2].

In this research, binder-free carbon aerogel electrodes were synthesized by sol-gel polycondensation of resorcinol with formaldehyde followed by drying at ambient pressure, and carbonization. Synthesis conditions of resorcinol formaldehyde (RF) carbon aerogels, such as catalyst concentration, water content, and gelation temperature, play an important role in controlling the structure, bulk density, and mechanical properties of carbon aerogel [3] fast and cost-effective method for monolithic carbon aerogels (CAs and were adjusted to obtain stable structure, which can be used as an electrode without binder.

The surface morphology and porous structure of the obtained carbon aerogels were examined by scanned electron microscope (SEM) and energy-dispersive X-ray diffraction (EDX) analysis. The applicability of these materials as electrodes in supercapacitors was investigated using electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and galvanic charge/discharge (GCD) measurements in a conventional three-electrode cell with 6M KOH aqueous electrolyte, employing a PalmSens4 potentiostat.

The prepared electrodes exhibited quasi-rectangular, symmetric, and reversible CV curves, indicating excellent electrochemical properties and, thus, the applicability of the binder-free carbon aerogels-based electrodes for high-performance capacitors. The triangular shape observed in the GCD curves within the range of –1 to 0 V further confirms the retention of these exceptional electrochemical properties

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# METHOD DEVELOPMENT AND COMPARATIVE EVALUATION OF FLUORESCENCE DETECTION IN HPLC AND SFC FOR TOCOCHROMANOL ANALYSIS IN OILS AND SEED EXTRACTS

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Supercritical fluid chromatography (SFC) offers several advantages, including reduced viscosity of the mobile phase, alternative separation selectivity, environmental sustainability, and decreased operator exposure to hazardous organic solvents. Fluorescence detection (FD) allows for sensitive and selective determination, but conventional flow cell designs are incompatible with SFC. A high-pressure flow cell specifically for SFC has been available for over a decade but is underutilized. Tocochromanols are lipophilic antioxidants with a fluorophore, allowing FD without derivatization. The high sensitivity of FD is crucial for the analysis of tocochromanols, given their low abundance in plant matrices. The determination of these compounds holds significant relevance in various scientific disciplines, including phytochemistry, food science, pharmaceuticals, and agriculture.

This research focuses on the development of the SFC-FLD method for the determination of nine tocochromanols, specifically PC-8 and α-, β-, γ-, and δ- tocopherols and tocotrienols. The chromatographic selectivity and resolution behaviour of tocochromanols were evaluated using eight different columns, alongside an assessment of the impact of injection volume on the peak shape. The developed SFC-FLD method employed gradient elution utilizing $CO_2$ and methanol as mobile phase components, with two amino columns connected in series. Sensitivity comparisons were made between the SFC-FLD-DAD method and the NPLC-FLD-DAD method. The sensitivities of SFC-DAD, SFC-FLD, NPLC-DAD, and NPLC-FLD were found to be 58.6–160.9, 5.9–51.9, 19.7–63.5, and 0.42–4.3 pmol, respectively. This developed method was successfully applied to analyse seed ethanol extracts and oils diluted in 2-propanol.

**Acknowledgements**. This research was funded by the Latvian Council of Science, project "Dicotyledonous plant families and green tools as a promising alternative approach to increase the accessibility of tocotrienols from unconventional sources", project No. lzp-2020/1-0422.

# EXPLORING ATOMIC FORCE MICROSCOPY FOR EX VIVO CHARACTERIZATION OF HUMAN LUNG CANCER TISSUE HISTOLOGY SAMPLES

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Studying lung cancer is crucial due to its high incidence and mortality rates worldwide, making it one of the leading causes of cancer-related deaths [1]. Understanding the disease's progression at cellular and molecular levels could improve diagnostics, personalized treatments, and patient outcomes. Atomic Force Microscopy (AFM) provides a unique tool to study lung cancer tissue morphology at the nanoscale, providing insights into surface topography, mechanical properties, and structural changes in cancer cells and the extracellular matrix. Advancements in machine learning (ML) further enhance AFM's potential by enabling automated analysis of large datasets, improving the accuracy and speed of identifying key biomechanical properties. For example, recently ML techniques have been adapted to study correlations of AFM biophysical data to clinical and histopathological data [2].

This work explores the potential of AFM as a complementary tool in lung cancer diagnostics, focusing on high-resolution imaging and characterization of histology samples from lung adenocarcinoma and squamous cell carcinoma. Unlike traditional studies that often rely on specially prepared samples or cultured cells, our approach utilizes routine intraoperative frozen histology samples without additional sample preparation.

In this work, we discuss the potential of AFM to reveal ultrastructural details beyond the resolution of conventional microscopy. AFM was employed to investigate structural and morphological differences between tumor cell regions and stroma. It was also used to analyze and compare cellular features of cancerous cells, as well as assess extracellular matrix components such as collagen fibrils. Surface roughness tests were employed to compare adenocarcinoma, squamous cell carcinoma, and control samples, aiming to identify potential differences in tissue structure.

**Acknowledgements**. This study was conducted with the financial support from the Recovery and Resilience Facility (Project No. 5.1.1.2.i.0/1/22/A/CFLA/002), within the framework of the project of Competence Center of Electrical and Optical Equipment Production Sector of Latvia.

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# MECHANOCHEMICAL CONTROL OF CAFFEINE – ANTHRANILIC ACID COCRYSTAL POLYMORPHS: INFLUENCE OF ADDITIVES ON POLYMORPHIC OUTCOMES

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Many solids exhibit polymorphism, an ability of a substance to exist in different solid crystalline forms. These variations often result in different characteristics, including melting point, hygroscopicity, stability, and solubility [1]. Since the solubility of many drugs is limited, there is a need to find ways how to improve this property. Multicomponent crystalline solid systems, such as cocrystals, have garnered significant interest, as their formation presents a promising strategy for modifying the solubility and dissolution rate of drugs [2].

In this study we employed mechanochemical synthesis of co-crystals, by exploring the possibility to control the obtained crystal form of the caffeine : anthranilic acid (Figure 1) co-crystal.

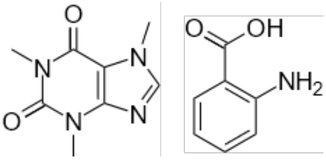

*Figure 1.* Molecular structure of caffeine (on the left) and anthranilic acid (on the right)

Various methods were studied for this system: Neat grinding, Liquid assisted grinding (LAG) with pure solvents as additive, LAG using other solid and liquid additives, LAG with pure solvents and other liquid additives and Neat and liquid grinding with additives (surfactants). As well as cooling crystallization and suspension for comparison. All 3 polymorphic forms can be obtained using only span20 and nitromethane. With nitromethane it is mechanochemically possible to obtain both polymorphic form I and II, also in combination of nitromethane and span20 both, it is possible to obtain form I, only with span20 – form III.

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# MONTMORILLONITE – IRON(III) HEXACYANOFERRATE(II) COMPOSITE: CO-SYNTHESIS, PROPERTIES AND APPLICATIONS

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Montmorillonite ($(Na,Ca)_{0.33}(Al,Mg)_2(Si4O_{10})(OH)_2 \cdot nH_2O$) – a naturally occurring aluminosilicate mineral, consists of tetrahedral ($SiO_4$) and octahedral ($AlO_6$) sheets in a 2 : 1 layer arrangement. Its high surface area, swelling capacity, low toxicity, adsorption properties, and bactericidal and hemostatic abilities make it a promising material for biomedical applications.

Iron(III) hexacyanoferrate(II) ($Fe_4[Fe(CN)_6]_3 \cdot nH_2O$) efficiently binds cesium and other toxic radionuclides and ions due to its unique structural configuration. Co – synthesis combines montmorillonite's structural versatility with the radionuclide – binding efficiency and potential photothermal properties of iron(III) hexacyanoferrate (II), expanding its applications in environmental and biomedical fields.

Montmorillonite was precleaded by washing with deionised water to remove soluble impurities followed by modification with several (2M NaOH) and acid (2M $H_2SO_4$) treatment methods. These modified samples served as matrices for co – synthesizing iron(III) hexacyanoferrate(II) and montmorillonite composites via liquid – phase, hydrothermal and solid – phase methods. Preliminary results showed that the solid – phase composites had superior cesium adsorption efficiency and rate compared to Radiogardase® Cs (see Table 1), highlighting their potential for radionuclide – binding wound dressings with hemostatic properties.

*Table 1.* Instant Cs sorption efficiency in the presence of Co and Sr ions (0.01 mg/mL Cs solution)

| **Sample** | **Instant Cs sorption efficiency, % (± SD)** |
|---|---|
| Montmorillonite (acid-modified) | 12.6 ± 4.5% |
| Radiogardase Cs® | 32.4 ± 2.8% |
| Iron(III) hexacyanoferrate(II) synthesized via mechanical synthesis | 66.6 ± 1.3% |
| Montmorillonite (alkali-modified) | 74.4 ± 0.9% |
| Montmorillonite (acid-modified) / iron(III) hexacyanoferrate(II) composite | 93.0 ± 0.3% |
| Montmorillonite (alkali-modified) / iron(III) hexacyanoferrate(II) composite | 98.7 ± 0.1% |

Advanced characterization methods, including XRD, FTIR, BET, BJH, XRF, EDX and laser scattering for particle size and zeta potential, are essential for a comprehensive understanding of the properties of these novel hybrid composites.

This study presents an innovative strategy for the development of multi-functional materials with considerable potential in biomedical, pharmaceutical and environmental applications through the co – synthesis of montmorillonite and iron(III) hexacyanoferrate(II).

**Acknowledgements**. The authors express their gratitude to Keramserviss Ltd for providing the montmorillonite used in this study, with special appreciation to Irina Jezova for her dedicated support.

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# PEO METHOD AS AN ALTERNATIVE TOWARDS CARBONATE AND APATITE COATINGS – A REVIEW OF CURRENT STATE OF ART

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Bioactive implant coatings on metal bases are crucial in contemporary biomedical engineering, offering both short-term and enduring solutions for restoring bone and teeth impairments. Coatings integrating calcium carbonate (CC) and hydroxyapatite (HA) are especially efficient in replicating natural calcified tissues, engaging the principles of fourth-generation biomaterials. Existing methodologies largely limit the advancement of fully functional CC-HA coatings. Simultaneously, plasma electrolytic oxidation (PEO), one of the most promising techniques for chemical modification of metallic surfaces (Figure 1), remains insufficiently explored in relation to carbonates [1].

This research thoroughly examined the obstacles and constraints linked to the simultaneous incorporation of CC and HA into PEO coatings, emphasizing the additives' physical state, physicochemical attributes, synthesis approaches, and PEO process variables. Furthermore, an optimal methodology for fabricating Ti-based CC/HA coatings was systematically determined through a deductive framework and causal assessment. Conventional PEO baths containing only soluble ingredients were deemed unsuitable, whereas those involving two-phase particle suspensions demonstrated explicit benefits for the intended purpose.

The ultimately favored bath formulation consisted of a CC particle suspension synthesized through a carbonation pathway and subsequently subjected to competing dissolution-precipitation and chemisorption reactions in a dibasic sodium phosphate electrolyte. In conclusion, the present study established a robust conceptual foundation for the practical application of CC/HA PEO coatings.

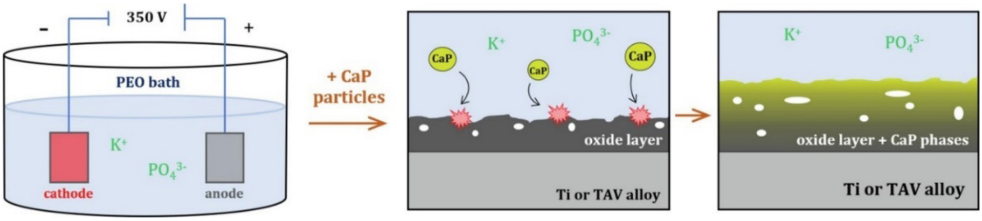

*Figure 1.* Schematic diagram of plasma electrolytic oxidation process for bioactive coating fabrication, used under Creative Commons CC-BY license

**Acknowledgements**. This work was financed by the Silesian University of Technology with the grant number 04/010/BKM24/1087.

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# Cu(II) AND Cd(II) HEAVY METALS SORPTION CAPACITY OF MYCELIUM BIO-COMPOSITES MODIFIED WITH CHITOSAN

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Chitosan is a low-cost biosorbent with a high heavy metal adsorption capacity. However, its primary limitations include solubility in acidic solutions and a nonporous structure. [1] Integrating chitosan into mycelium-based bio-composites offers a sustainable and eco-friendly alternative to the chemical modification of chitosan-based sorbents.

The effect of the incorporation of chitosan into birch sanding dust (BSD) mycelium bio-composites on the sorption of heavy metals was studied. The BSD samples with different chitosan content were characterized by functional group, and porous structure analyses (specific surface area ($S_{BET}$) and total pore volume). Cu(II) and Cd(II) metals equilibrium sorption capacity ($q_e$) were determined by using the flame atomic absorption spectrometer AAnalyst-200. The sorption kinetic of heavy metals was studied. Results are shown in Table 1.

*Table 1.* Specific surface area ($S_{BET}$), total volume of pores and equilibrium sorption capacity ($q_e$) of Cu(II) and Cd(II) on birch sanding dust (BSD) mycelium bio-composites

| Sample | $q_e$, mg(Cu)/g | $q_e$, mg(Cd)/g | $S_{(BET)}$, m$^2$/g | V, cm$^3$/g |
|---|---|---|---|---|
| Birch sanding dust | 1.5 ± 0.4 | 0.8 ± 0.1 | 1.4 ± 0.1 | 3.10 ± 0.06*10$^{-3}$ |
| BSD – 0% | 2.0 ± 0.1 | 0.73 ± 0.05 | 3.3 ± 0.4 | 5.0 ± 0.3*10$^{-3}$ |
| BSD – 2% | 2.57 ± 0.06 | 0.802 ± 0.004 | 2.8 ± 0.5 | 4.1 ± 0.6*10$^{-3}$ |
| BSD – 4% | 2.78 ± 0.02 | 0.98 ± 0.05 | 2.7 ± 0.1 | 3.98 ± 0.09*10$^{-3}$ |
| BSD – 10% | 4.26 ± 0.04 | 0.95 ± 0.16 | 2.6 ± 0.2 | 3.9 ± 0.2*10$^{-3}$ |
| BSD – 15% | 4.74 ± 0.05 | 1.32 ± 0.14 | 2.04 ± 0.03 | 3.82 ± 0.04*10$^{-3}$ |

There is a negative correlation between chitosan content in the BSD and both the surface area and volume of the samples (Pearson's correlation coefficient $\rho$ are –0.92 and –0.73, respectively), the BET surface area and pore volume decrease, indicating, that chitosan addition leads to a less porous composite structure. Simultaneously, the equilibrium sorption capacity of Cu(II) and Cd(II) increased. Additionally, pH decreased after sorption on average from 5.4 to 4.5 for Cu(II) solution and from 6.0 to 4.9 for Cd(II) solution respectively. That clearly indicates proton exchange and chemisorption.

The obtained results clearly showed that the incorporation of chitosan is a perspective way to improve biosorbent (mycelium bio-composite) heavy metal sorption capacity; however, chitosan decreased sorbent porous structure.

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# SIMULTANEOUS DETERMINATION OF $C_{10-17}$ POLYCHLORINATED ALKANES IN FOOD BY A LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY METHOD

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Polychlorinated n-alkanes (PCAs) are a complex group of persistent substances that make up most chlorinated paraffin (CP) mixtures. and are widely produced and used as plasticizers and lubricants in packaging and appliances, causing environmental and food contamination concerns [1]. Reports say that long-term exposure to PCAs could be toxic to living organisms, causing oxidative stress, disturbances in energy metabolism and even cancer [2]. Homologues of one group (PCAs-$C_{10-13}$) are classified as persistent organic pollutants (POPs); however, due to similar properties, studies suggest that their replacements could also potentially be toxic to living organisms. Therefore, the applications of PCAs-$C_{14-30}$ could be restricted, and this would cause a need for practical, reliable and widely accessible analysis methods [3].

This study aimed to develop a liquid chromatography-electrospray ionization-tandem mass spectrometry (LC-ESI-MS/MS) method for PCA analysis in food products. Initially, we evaluated five analytical columns and different gradient settings to identify the most suitable stationary phase and gradient parameters for achieving adequate separation between homologues. Subsequently, we optimized the parameters and homologue fragmentation paths for tandem mass spectrometry. A comparative analysis was conducted to verify method performance. Reference materials such as lard and fish tissue from the Joint Research Center were used to evaluate the method. In addition, various food samples from different matrices were analyzed to study the occurrence of PCAs in food. The results from the developed LC-ESI-MS/MS method were then compared with those obtained from the liquid chromatography-electrospray ionization-high resolution mass spectrometry (LC-ESI-HRMS) method.

The results demonstrated that the developed LC-ESI-MS/MS method successfully analyzed PCA homologues – reference material results had acceptable Z-scores. Additionally, the method performance was comparable to that of the LC-ESI-HRMS method, confirming that the developed LC-ESI-MS/MS method is suitable for food sample analysis.

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# THERMOELECTRIC PROPERTIES AND APPLICATIONS OF AQUEOUS ELECTROLYTE INFILTRATED IN ANODIC ALUMINIUM OXIDE NANOCHANNELS FOR ENERGY HARVESTING

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The ongoing global decarbonisation trend has attracted much attention to more sustainable energy sources that would reduce dependance on fossil fuels. Direct conversion of heat to electricity is one of the main ways to satisfy the increasing energy demand and minimise carbon dioxide emissions. Waste heat generated as a by-product of various processes is typically considered to be at a temperature of approximately below 100 °C, and this type of thermal energy is produced and released into the environment from various natural and industrial processes, power plants, household electronic equipment and even human body. The development of a new nanofluidic platform technology based on the ion transfer in nanofluidic membranes would lead to a breakthrough in flexible and sustainable energy harvesting and storage. To accomplish this goal, it is essential to develop precisely engineered nanofluidic membranes to generate a significant thermovoltage, *i.e.* a high ionic Seebeck coefficient, when a temperature difference is applied, by confining ion transport in charged nanochannels.

Nanoporous anodic aluminum oxide (AAO) is one of the most popular and cost-effective materials due to its ease of fabrication, excellent thermal stability, high-density arrays of nanochannels and the ability to precisely control the morphology of these nanochannels. The synthesis of AAO membranes can be applied not only for production of thermoelectric devices, but also other applications such as templates, molecular separation etc.

In this work, a nanofluidic platform was developed using AAO membranes with a pore diameter of 25 nm and thickness of 50 microns, infiltrated with $Na_2SO_4$ aqueous electrolyte of different concentrations, to implement ion transport and energy generation by converting electrokinetic and thermal energy into electricity. To test the thermoelectrical properties of aqueous electrolyte-infiltrated AAO membranes, a sandwich-type cell was designed. Applying a temperature difference to the cell showed an increase in output voltage due to thermally driven ion transport in the nanochannels, with a tendency to decrease in aqueous electrolytes of higher concentration. The dependence of the output voltage per Kelvin obtained from the thermodiffusion of ions inside the nanofluidic membrane on the electrolyte concentration could be used to investigate the contribution of electrokinetic effects that occur in nanochannels.

# EVALUATION OF THERMAL STABILITY AND STRUCTURAL CHANGES OF 3-NITROBENZANTHRONE DURING ANNEALING IN VACUUM AND AIR

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Benzanthrone-based dyes have been a topic of interest in various fields, e.g., biomaterials and helminthology, due to their luminescent properties.[1] However, thermal stability and structural changes of newly synthesised derivatives have not been fully characterised; therefore, their application in previously mentioned fields is still in the research stage. In this research, the benzanthrone derivative 3-nitrobenzanthrone (3-$NO_2$BA) has been analysed before and after thermal annealing in various conditions. Dye samples have been annealed at different temperatures in vacuum and air, and the resulting powder samples have been characterised by attenuated total reflectance – Fourier transform infrared (ATR-FTIR) spectroscopy and other relevant methods to evaluate thermal stability and structural changes.

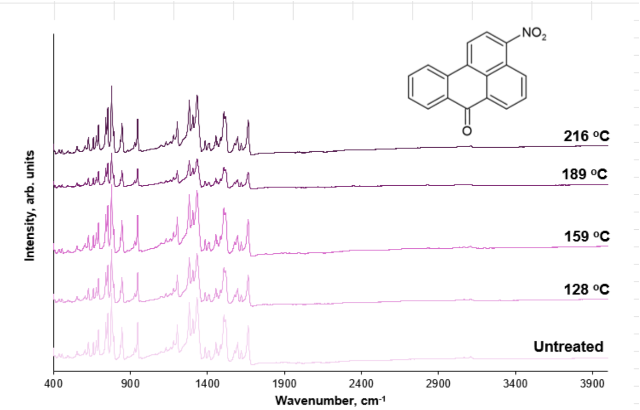

*Figure 1.* ATR-FTIR spectra of 3-$NO_2$BA sample before and after annealing at various temperatures in vacuum

The obtained results indicate that during annealing up to 216 °C in vacuum, no significant structural changes have been observed for the 3-$NO_2$BA sample using

ATR-FTIR spectroscopy. Minor structural changes can probably be related to the sample reactions with oxygen from air. Evaporation of the sample has been observed after annealing at 242 °C in vacuum, while in air at that temperature, only slight charring/visual changes were observed.

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# GREEN CHEMISTRY-BASED PROCESSING OF SPRUCE GREENERY FOR SUSTAINABLE INDUSTRIAL USE

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Latvia's forestry sector is a crucial component of its bioeconomy, with forests covering approximately 52% of its territory. Norway spruce (*Picea abies L.*) accounts for about 25.5% of the total forested area, making it one of Latvia's dominant commercial tree species [1]. While the timber industry efficiently utilizes spruce wood, the potential of spruce greenery comprising needles, twigs, and bark, remains underexploited. These by-products contain valuable bioactive compounds, including polyprenols, flavonoids, polyphenols and waxes, which have applications in pharmaceutical industry, cosmetics, and agriculture [2, 3].

This study aims to optimize a green extraction method for spruce greenery, focusing on solvent selection, process efficiency, and bioactive compound stability. By replacing harmful solvents with sustainable alternatives, the study focuses on improving industrial scalability while minimizing environmental impact. The results of this research will contribute to developing high-value bioproducts from forestry residues, supporting circular economy principles in Latvia's bioeconomy.

Preliminary results show that it is possible to use isopropanol to replace the use of nephrase in extracting spruce greenery to obtain total extractables. So far, biomass extraction using glycerol and propylene glycol was optimised yielding higher polyphenolic, antiradical and antioxidant activities, compared to isopropanol extracts. By developing different biorefining schemes, it is possible to adapt to various industrial sectors depending on their needs.

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# MOLECULAR ENVIRONMENTAL FILTERS BASED ON SBA-15 FOR THE SORPTION OF SILVER AND COBALT IONS

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Heavy metal pollution negatively impacts flora and fauna, as these toxins are present in soil and water, facilitating their accumulation in drinking water and plants. Chronic exposure to heavy metals can lead to health issues, including cardiovascular dysfunction and cancers. Current purification methods are costly and inefficient. A proposed solution is mesoporous silica SBA-15, which acts as a molecular sieve, effectively absorbing metals from contaminated soils and waters while being non-invasive and environmentally friendly [1]. SBA-15 is characterized by a hexagonal arrangement of cylindrical mesopores with a diameter of 5 nm and micropores in the wall structure. SBA-15 exhibits exceptional mechanical, chemical, and thermal stability and a high specific surface area [2].

The research utilized mesoporous silica SBA-15 containing propyl-carboxyl groups at different concentrations of 1.25%, 2.5%, 5%, 10%, and 20%. The presence of active groups in the silica matrix enables selective adsorption of silver or cobalt ions depending on the changing environmental conditions. To evaluate the adsorption potential of the functionalized SBA-15 matrices, adsorption studies of silver and cobalt ions were conducted from a kinetic perspective using ICP-MS. The adsorption processes were carried out at different pH values (pH 5, 7, and 9). Appropriate kinetic models (including PFO, PSO, PNO, and IPDM) were selected to verify the sorption processes in the studied materials.

The obtained research results allowed for the determination of the optimal pH for the sorption of silver ions and cobalt ions depending on the concentration of active groups in the matrix. The applied propyl-carboxyl groups exhibit increased sorption potential for silver ions compared to cobalt ions. Depending on the concentration of active groups and the pH of the environment, the material can be selected for specific sorption applications. The most efficient adsorption of cobalt ions occurs at pH 9 for samples containing 20% functional groups and at pH 5 for samples with 1.25% active group content. In contrast, the most efficient process for silver ions was recorded depending on the pH for samples containing 20% (pH 5), 5%, and 2.5% (pH 7), as well as for samples with 1.25% active groups in pH 9.

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# POLYPHENOL CHARACTARIZATION AND ANTIOXIDANT ACTIVITY OF RIBES NIGRUM BERRY PRODUCTS

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*Ribes nigrum* (Blackcurrant) berries are abundant in antioxidants, therefore, whole berries and their products, like juice, are widely used in the food industry [1]. As a side-product pomace are often discarded, but recently gain interest [2]. The aim of our study was to compare polyphenol composition and their antioxidant potential in berries, juice and pomaces.

Berries, juice and pomaces were extracted using ethanol of different concentrations (50%, 70% and 96%), then freeze-dried. Total phenolic content (TPC), DPPH antiradical activity was determent. High precision liquid chromatography (HPLC-UV) was used to characterise phenolic acids, flavonoids and anthocyanidins.

The pomaces were the most abundant in polyphenols (62mg/100g extract of gallic acid equivalent (GAE)), in comparison the juice had almost two times less of the phenolic compounds (27 mg / 100 g extract GAE). The 70% ethanol extract of berries had the highest phenolic content (46 mg / 100 g extract GAE) compared to 50% and 96% ethanol extracts (37 mg and 34 mg, respectively). The antioxidant activities were different for all analysed products.

The preliminary data from HPLC analysis showed that although similar compounds were detected in all extracts, the pomaces were the richest in phenolic acids, flavonoids and anthocyanidins. In addition, ethanol concentration effected polyphenol profile of berry extracts.

In conclusion, pomaces are valuable source of polyphenols and need to be analysed further for pharmaceutical applications.

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# SECTION OF ORGANIC CHEMISTRY

# 5-TRIAZOLYL URIDINE IMPROVES NUCLEOBASE STACKING AND PYRIMIDINE RECOGNITION IN RNA-BINDING TRIPLEX-FORMING PEPTIDE NUCLEIC ACIDS

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Peptide nucleic acid (PNA) is a neutral DNA analog uniquely fit for triple helical recognition of nucleic acids. However, the practical applications of triplex-forming PNAs have been limited by sequence restriction on recognition target as stable base triples are formed only with the purine bases.

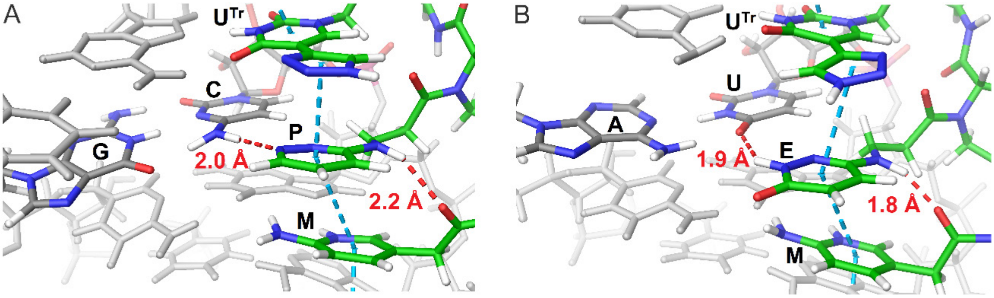

*Figure 1.* (A) P•C-G and (B) E•U-A triples

The present study explores a new way to improve pyrimidine recognition by enhancing nucleobase stacking in the PNA strand. Placing 5-triazolyl uridine next to the modified nucleobases designed for Hoogsteen recognition of pyrimidines in double helical RNA increased the binding affinity while maintaining good sequence specificity. Molecular dynamics simulations confirmed that the beneficial effect was due to synergistic stacking interactions between the triazole and neighboring modified nucleobases. The increased binding affinity improved biological activity of triplex forming PNAs targeting microRNA precursor hairpin in a cell-based dual fluorescent protein assay. The results demonstrate a new approach to address the problem of pyrimidine recognition that has been a key bottleneck for Hoogsteen triple helical targeting of nucleic acids.

# DEVELOPMENT OF MOF-LUMINOPHORE FOR SOLID-STATE GAS SENSOR APPLICATIONS

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In recent years solid state organic luminophores have garnered attention for their potential uses in light-emitting diodes because of their low cost of production. One of the breakthroughs in solid-state organic luminophores was the discovery made by K. Leduskrasts in 2019 [1] where solid-state luminescence was achieved by utilizing $\pi^+ - \pi$ interactions in a pyridinium – carbazole system. Further research by K. Leduskrasts and his team led them to discover the structure of luminophore **1** and its derivatives achieving quantum yields up to 85%. [2]

In collaboration with the Institute of Atomic Physics and Spectroscopy, we've found that luminophore **1** changes optical properties when exposed to ammonia and acetic acid vapors, which suggests their potential use as a solid-state gas sensor. Our recent findings indicate that a possible mechanism of interaction happens on the luminophore's surface layer. This led us to develop a composite material **3** where the increase of surface area is achieved by linking the organic luminophore **1** to a metal-organic framework (MOF) **2** (Figure 1).

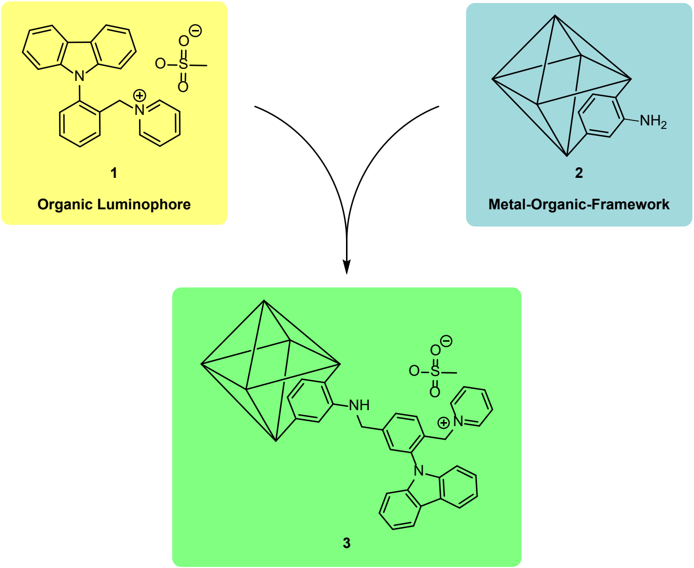

*Figure 1.* Development of MOF-luminophore 3

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# SYNTHESIS OF POLYMER SUPPORTED CATALYSTS: TOWARDS ACYLATIVE DKR OF SECONDARY ALCOHOLS IN CONTINUOUS FLOW

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Dynamic kinetic resolution (DKR) is a powerful synthetic method for obtaining enantioenriched secondary alcohol derivatives from racemic alcohols. This is achieved by employing two parallel processes – selective functionalization of one enantiomer and simultaneous racemization of the slower-reacting enantiomer (Figure 1).

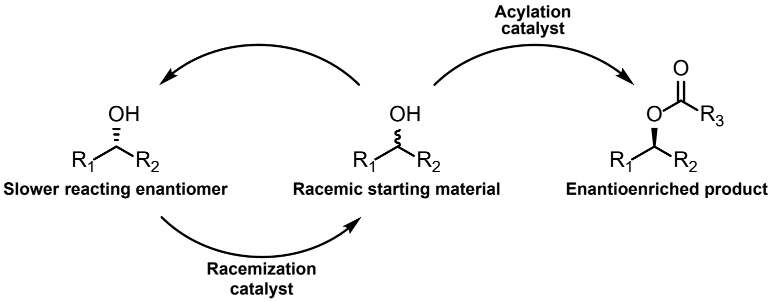

*Figure 1.* Acylative DKR of secondary alcohols

However, only a handful of nonenzymatic DKR methods exist for this transformation [1, 2, 3]. The scarcity of acylative DKR protocols stems from the fact that Ru racemization catalysts are inactivated by forming a complex with various DMAP-type acylation catalysts. One of the ways this problem can be circumvented is by attaching the catalysts to an insoluble polymer support, thereby allowing the separation of the acylation and racemization processes. This would also enable the DKR to be performed in continuous flow thereby facilitating the purification of products and enabling the repeated use of the catalysts.

Herein we present novel polymer-supported catalysts. The catalysts have been tested in the enantioselective acylation reaction and the racemization reaction of secondary alcohols. Preliminary results show that the polymer supported Ru racemization catalyst has low stability under continuous flow conditions.

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# DEVELOPMENT OF ARYLBORONIC ACIDS AS REVERSIBLE COVALENT INHIBITORS OF PLASMODIUM SERINE PROTEASE SUB1

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Malaria is a disease which causes over 600 000 deaths annually. It is caused by the *Plasmodium* parasite – a unicellular organism which can infect and replicate in human erythrocytes. A subtilisin-like serine protease SUB1 is pivotal in the parasites escape from the infected cell making it an attractive anti-malarial drug target. Previously we reported that boronic acid **1** acts as an inhibitor of SUB1 by forming a covalent reversible bond with a serine residue in the catalytic site of the enzyme [1]. In this work we decided to replace the amide bond at the $\mathbf{P_1–P_2}$ position with a substituted aryl moiety to modify the physiological properties (solubility, lipophilicity, stability) of compound **1** (Figure 1).

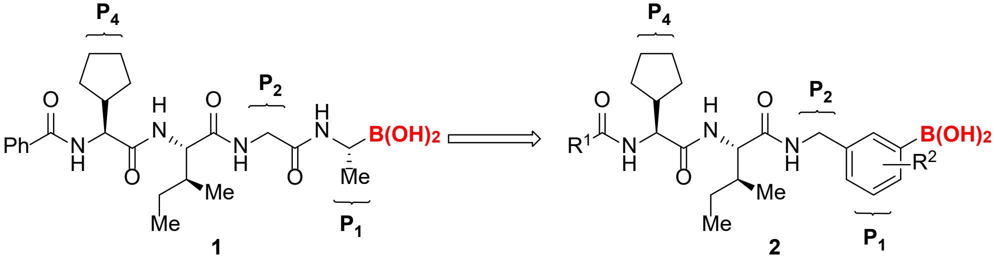

*Figure 1.* Depeptidization of $P_1$-$P_2$ position

**Acknowledgements**. This project is funded by Recovery and Resilience Facility (RRF grant No. 21/OSI/DG) and by student grant from Latvian Institute of Organic Synthesis (IG-2025-09).

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# COPPER-CATALYZED ARYLATION AND SUBSEQUENT CYCLIZATION OF TERMINALLY FUNCTIONALIZED PROPARGYL SILANES

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Recently we have published synthesis methods for propargyl silane 1,3-difunctionalization with concomitant silyl shift [1]. The concept involves propargyl silane activation with an electrophile, followed by a 1,2-silyl shift. This creates an electrophilic carbon center that can react with a nucleophile. This work presents the use of hypervalent iodine(III) reagents as formal carbon electrophiles to activate the propargyl silane moiety. The reaction proceeds via formation of the aryl cuprate from diaryliodane, which activates the propargyl silane to undergo the 1,2-silyl shift. This generates a carbenium ion or its equivalent, which is trapped by the internal nucleophile (alcohol or amide) present. A variety of aromatic groups with electron donating and electron withdrawing substituents was successfully applied in this reaction, as well as some heteroaromatic groups.

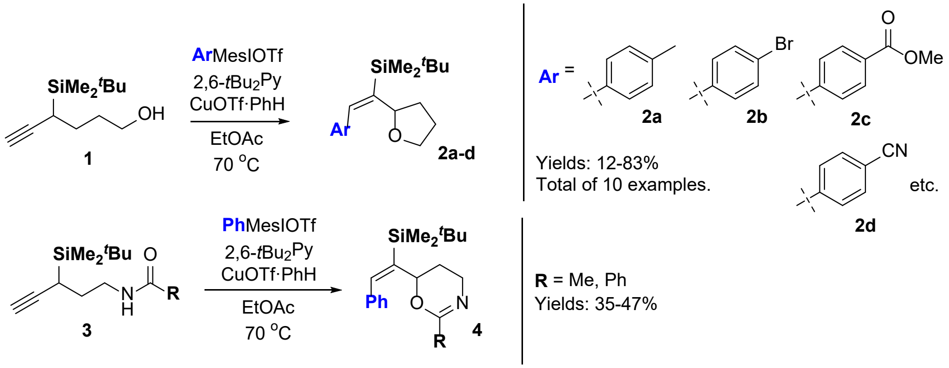

*Figure 1.* Arylation-cyclizaton of propargyl silanes under copper-catalyzed conditions

**Acknowledgements**. The Latvian Council of Science Grant LZP-2023/1-0576 is kindly acknowledged for financial support.

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# SYNTHESIS OF WATER SOLUBLE PENTACYCLIC TRITERPENOID PHOSPHONATES

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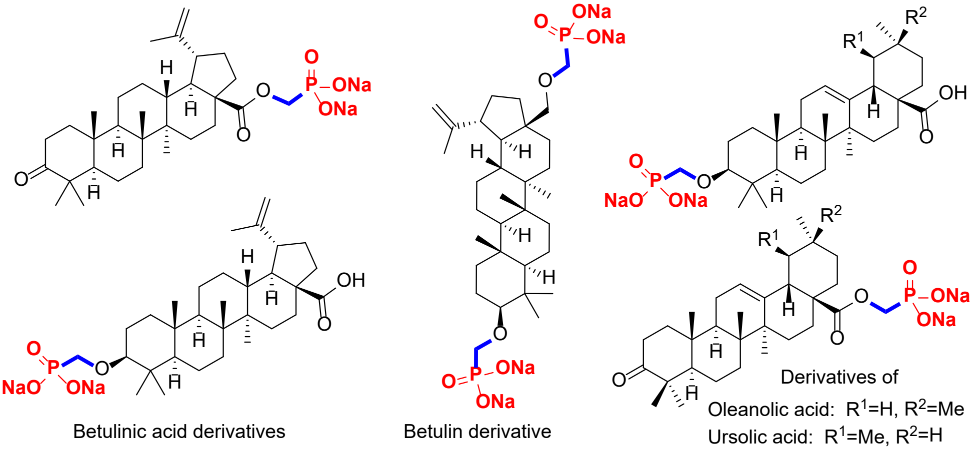
Natural pentacyclic triterpenoids are important secondary metabolites that have attracted interest due to the wide range of their biological activities such as antitumor [1], antidiabetic [2] and antiviral activities [3]. Oleanolic, ursolic acids and betulin, are the most recognizable compounds of this branch, which are isolated from various plants. However, the medicinal application of these natural products are hindered by their extremely low water solubility and thus – low bioavailability [4]. One option to overcome this limitation is introduction of polar anionic functional groups such as phosphates and sulfates, which, however, are prone to hydrolysis.



Betulinic acid derivatives

Betulin derivative

Derivatives of
Oleanolic acid: $R^1$=H, $R^2$=Me
Ursolic acid: $R^1$=Me, $R^2$=H

*Figure 1.* Desired target compounds

Here we describe the synthesis of novel anionic triterpenoid phosphonates [5], which bear methylene-bridged phosphonate side chains. The latter are suitable for both the enhanced water solubility and complexing / salt formation with metal ions like $Ca^{2+}$, which is important for their further applications as bioactive additives to various calcium phosphate-based biomaterials.

**Acknowledgements**. Dr. A. Dubņika is acknowledged for the cell viability tests.

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# SYNTHESIS AND APPLICATION OF AMINO DERIVATIVES OF PENTACYCLIC TRITERPENOIDS

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Naturally abundant pentacyclic triterpenoids are important secondary metabolites, which have aroused huge interest by possessing wide range of remarkable biological activities such as antitumor [1] antidiabetic [2] anti-inflammatory [3] and antiviral activities [4]. Oleanolic acid and betulin are one of the most recognizable compounds of this branch, which are isolated from various plants.

The aim of this work is to obtain novel triterpenoid amino derivatives *via* C-H amination, forming new C-N bonds. For this purpose, precursors **1** and **2** bearing sulfamate directing groups were synthesized.

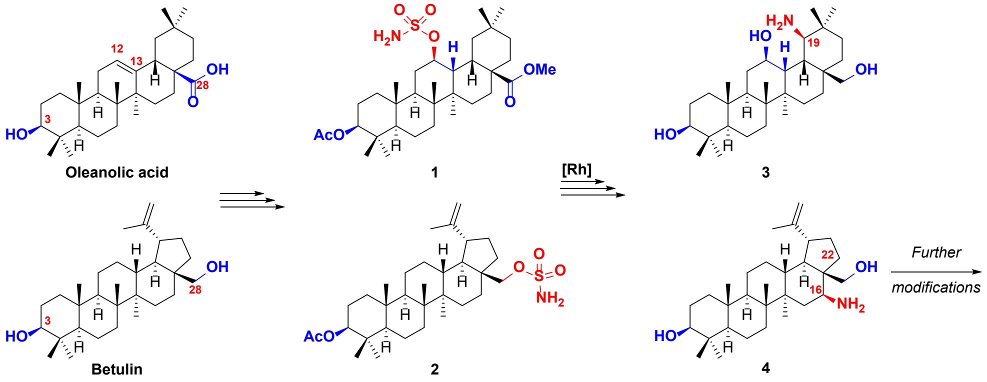

*Figure 1.* C-H amination of betulin and oleanolic acid

Obtained sulfamates **1** and **2** were treated according to Du Bois conditions and amino derivatives **3** and **4** were obtained [5]. Amine **4** proved to be useful in further modifications yielding triazoles, amino acids and secondary C-H amination products at C22.

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# PHOSPHORESCENCE IN ORGANIC CRYSTALS

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Phosphorescence has been widely observed from inorganic and metal containing luminescent materials (luminophores), which exhibit intense long-lived emission at great efficiencies. However, metal-based phosphorescent luminophores suffer from drawbacks such as high cost of production and toxicity, as well as low stability. In contrast to inorganic and metal containing luminophores, purely organic phosphorescent materials offer a cheap, stable and non-toxic alternative. Even though organic phosphorescent luminophores have been intensely studied for the last 20 years, their working mechanism is still under debate. In 2020 Liu and co-workers published a paradigm-shifting report where various previously known carbazole-containing phosphorescent luminophores were isolated in an ultra-pure form, and they did not display phosphorescence. Instead, the previously observed phosphorescence from the carbazole-containing luminophores was induced by a small amount of an isomeric benzo[*f*]indole impurity [1]. This discovery has led to increased interest in researching the role of impurities in the phosphorescence of purely organic materials. While numerous research groups have reported that impurities enable phosphorescence in specific organic compounds, this explanation has yet to gain widespread acceptance.

Herein, we show that ultra-pure organic materials, regardless of their structure, do not exhibit ultra-long phosphorescence. Organic materials that initially display ultra-long phosphorescence can be further purified using preparative RP-HPLC, yielding pure samples with negligible phosphorescence. Therefore, the presence of ultra-long phosphorescence in an organic material strongly indicates the presence of impurities.

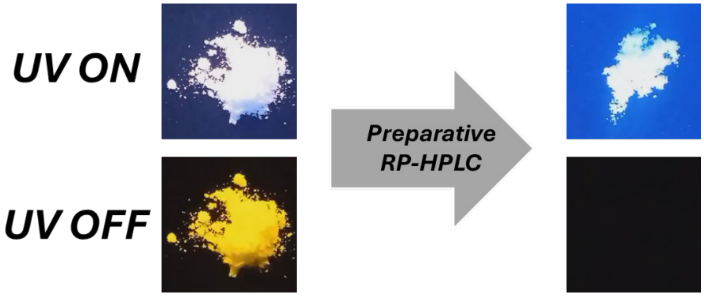

*Figure 1.* Disappearance of phosphorescence after preparative RP-HPLC of an organic material

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# CARBON-BASED RADICAL MEDIATED HALOGEN ATOM TRANSFER REACTION

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Halogen atom transfer (XAT) reactions have become a highly versatile and widely applicable method for forming carbon-carbon (C-C) bonds. Under XAT conditions, inexpensive and abundant feedstock chemicals can be converted into highly saturated molecules with diverse functional groups. However, traditional XAT reagents, such as stannanes and silanes, present significant challenges due to their toxicity and tendency for undesirable side reactions [1]. This has prompted ongoing research to identify safer and more efficient XAT mediators. Recently, carbon-based radicals have emerged as promising alternatives in this field [2].

In this study, unprecedented reactivity for a fluorinated carbon radical as a XAT mediator is demonstrated. We successfully transform simple unactivated alkenes and activated alkyl halides into products with a high $Fsp^3$ character through atom transfer radical addition. This method expands the range of products accessible via XAT reactions. Furthermore, mechanistic studies of key reaction steps provide valuable insights into the role of the fluorinated carbon radical in XAT, highlighting both the advantages and limitations of this novel approach. This work paves the way for future advancements in XAT chemistry.

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# SYNTHESIS OF CYCLIC BIARYL λ³-BROMANES VIA ELECTROCHEMICAL OXIDATION OF 2,2’-DIBROMOBIPHENYLS

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The synthesis of hypervalent bromine(III) compounds is much less studied and developed than their iodine(III) counterparts. Despite offering stronger oxidizing power, bromine(III) reagents are known for their lower stability and the need for toxic and highly reactive $BrF_3$ as a precursor in their synthesis [1]. Electrochemical methods represent a rapidly developing ecofriendly field in chemistry today, providing sustainable approaches for the production of organic compounds. We have found that cyclic symmetrical and non-symmetrical biaryl λ³bromanes **2** can be obtained in moderate yields by the two-electron anodic oxidation of 2,2’-dibromobiphenyls **1**. X-ray analysis of **2** shows that the bromane molecule exists in the form of an ionic pair and that the bromine(III) atom is stabilized by *ortho* carbonyl groups. Biaryl λ³bromanes with related structures are known to be used as aryne precursors under mild conditions or as halogen-bonding catalysts in Michael reaction [2, 3].

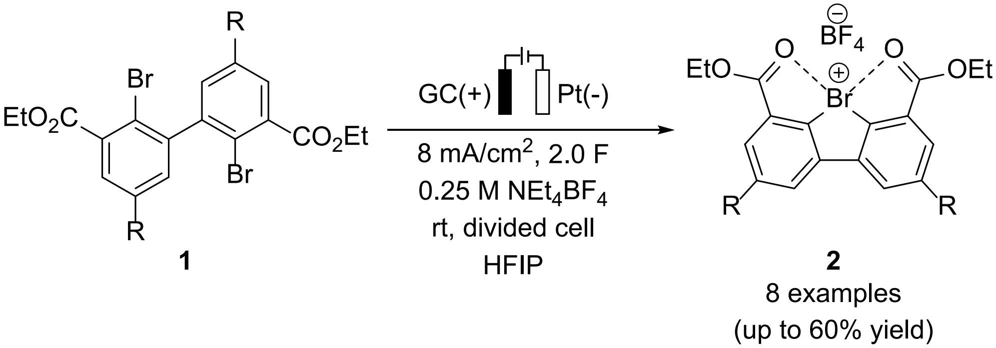

*Figure 1.* Electrochemical synthesis of λ3-bromane 2

**Acknowledgements.** This research was funded by the Latvian Science Council grant LZP2021/10595.

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# SYNTHESIS AND PROPERTIES OF 1-METHYL-3-(2,2,2-TRIFLUOROETHYL) IMIDAZOLIUM IONIC LIQUIDS

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Fluorination of ionic liquids (ILs) typically enhances their thermal stability, increases hydrophobicity, and alters key physicochemical properties such as viscosity, density, and thermal stability due to the unique electronegativity and steric effects of fluorine atoms. [1]

This work introduces a series of 1-methyl-3-(2,2,2-trifluoroethyl)imidazolium-based ionic liquids, featuring the anions bis(trifluoromethylsulfonyl)imide (TFSI), bis(fluorosulfonyl)imide (FSI), and triflate (OTf, **Figure 1**). Unlike the extensively studied non-fluorinated imidazolium ILs, the small, fluorinated cation used in this study has received limited attention, with no systematic investigations reported to date.

A combined synthetic work and property investigation of viscosity, density, and thermal stability reveals that these novel fluorinated ILs exhibit higher viscosity and increased density compared to their non-fluorinated 1-ethyl-3-methylimidazolium counterparts. These findings highlight the significant impact of the trifluoroethyl group on the physicochemical properties of ILs, offering new insights and potential applications in fields where enhanced viscosity and density of low-molecular weight ILs are required.

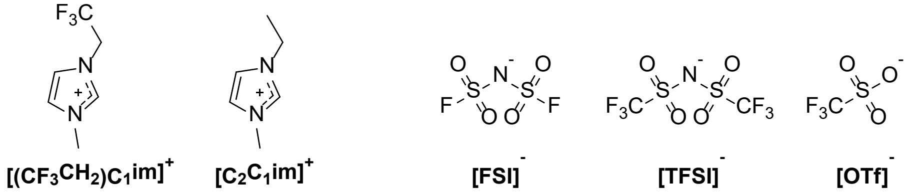

*Figure 1.* Ionic liquid ion structures studied in this work

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and IMSInstitute of Molecular Sciences (LA/P/0056/2020). R.M.A.S. is grateful to FCT for the award of his PhD grant (U1/BD/153093/2022).

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# ELECTROCHEMICAL DECARBOXYLATIVE SYNTHESIS OF α,α′-DIFLUOROESTERS

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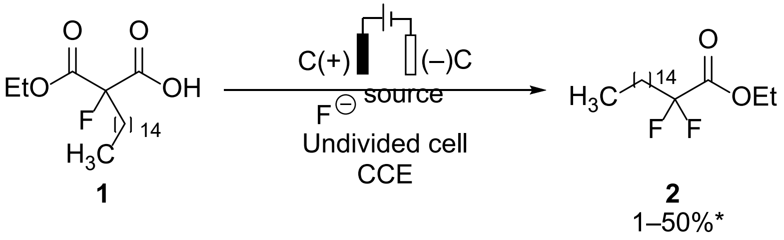
Fluorine is an important element of interest in the field of organic chemistry because of its similar size to hydrogen, higher electron-withdrawing capacity, and greater lipophilicity. Moreover, due to the strong nature of C–F bond as compared to C–H bond, efforts to manufacture fluoropharmaceuticals have increased in recent years [1]. Fluorine-18 containing compounds are also frequently used in positron emission tomography in both clinical and preclinical research accentuating the need for simple and efficient Fluorine-18 labelling procedures [2].

Recently, Markò *et al*. reported the anodic decarboxylation of malonic acid derivatives followed by the reaction with *in-situ* generated methoxide nucleophile, yielding ketals [3]. In the current research, the methoxide nucleophile is replaced with a fluoride nucleophile to afford α,α′-difluoroester **2** from α-fluorinated malonic acid monoester **1** and optimization of reaction conditions has been started.



*Yield determined by GCMS, using n-dodecane as internal standard.

*Figure 1.* Electrochemical synthesis of α,α′-difluoroester 2

The preliminary results show that fluorine containing, $Bu_4N\mathbf{PF_6}$ and $Bu_4N\mathbf{BF_4}$ salts and inexpensive inorganic fluorides can act as fluoride sources in the electrochemical decarboxylation/oxidation reaction, but further optimisation of reaction conditions is required.

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# INFLUENCE OF RADICAL INITIATOR AND MONOMER ON SORPTIVE PROPERTIES OF MOLECULARLY IMPRINTED POLYMERS (MIPS) FOR SELECTIVE SOLID-PHASE EXTRACTION OF CATECHOLAMINES AND THEIR METABOLITES

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Catecholamines (CAs, e.g. epinephrine, norepinephrine, dopamine) are important hormones and neurotransmitters present in human bodily fluids. Abnormal concentration of these compounds is linked to hypertension, cardiac arrythmia, neurodegenerative diseases (Parkinson's and Alzheimer's Diseases) and adrenogenic tumors (e.g. neuroblastoma). Simultaneous determination of CAs and their metabolites in urine and blood plasma can help quickly and reliably diagnose the aforementioned diseases [1].

Molecularly-imprinted polymers (MIPs) are synthetic receptors for a targeted molecule separation in a sample, offering high sample throughput and analyte selectivity under mild conditions. MIPs are made using radical polymerization in the presence of a template molecule (either a target molecule or its analogue) to create a matrix with shape-memorable cavities, allowing for selective analyte adsorption. Simultaneous isolation of CAs and their metabolites using solid-phase extraction (SPE) is a powerful approach with potential use in bioanalysis [2].

To evaluate recovery and dual molecular recognition for both CAs and their metabolites, MIPs were synthesized using a novel non-covalent approach by polymerizing *N,N'*-methylenebisacrylamide (MBAA, **2**) in presence of a salt formed by (4-vinylbenzyl)trimethylammonium (VBTMA, **1**) and homovanillyl alkoxide (**2**) or a salt formed by dihydroconiferyl alkoxide (**3**) and **1**, which act as dual-purpose templates/monomers for CAs. Another dual-purpose salt formed by **1** and homoveratric acid (**4**) was used for separation of acidic metabolites (VMA and HVA). AIBN (**5**) and V-65 (ADVN, **6**) were used as radical initiators for separate MIP batches. Templates **2** and **3** also were used in separate MIP batches.

MIP sorbents and corresponding non-imprinted control polymers (NIPs) with variable radical initiator loads were synthesized and packed into SPE cartridges. Standard analyte mixture containing CAs, their metabolites and common medications (salbutamol, dobutamine, ibuprofen etc.) was passed through. Imprinting factor (IF) and recovery figures for each compound (on MIPs) were calculated and compared to the corresponding NIPs. Preliminary results show that MIPs made using V-65 (**6**) and template **2** show better sorption selectivity (IF) but lower overall analyte recovery compared to MIPs that were made using AIBN (**4**) and **3**.

**Acknowledgements.** This work is supported by the Fundamental and Applied Research Project No. lzp-2022/1-0141.

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# PRELIMENARY RESULTS OF 4-METHYLENE γ-SULTINE ISOMER CONTROL BY THE CHOICE OF SULFUR DIOXIDE SOURCE

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Substrate structure and reaction catalyst determine selectivity of trimethylenemethane [3 + 2] cycloaddition reactions with any X = Y synthon, but, frequently, reactions yield isomer mixtures [1]. By tuning reaction conditions, for instance, varying catalyst, ligands and adding additives, desired product can be obtained with high selectivity [2].

While developing method for 4-methylene γ-sultine **2a,b** synthesis from methylenecyclopropanes **1a,b** (MCP's) and sulfur dioxide (Figure 1), our group noticed that use of 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (DABSO) with dialkyl- substituted MCP's **1b** yielded other sultine **3b** major isomer. Use of "free" sulfur dioxide (toluene solution) for the same substrates yields mainly non-isomerized sultine **2b**. Simply changing of $SO_2$ source enables convenient dialkyl- substituted sultine isomer selectivity reversal.

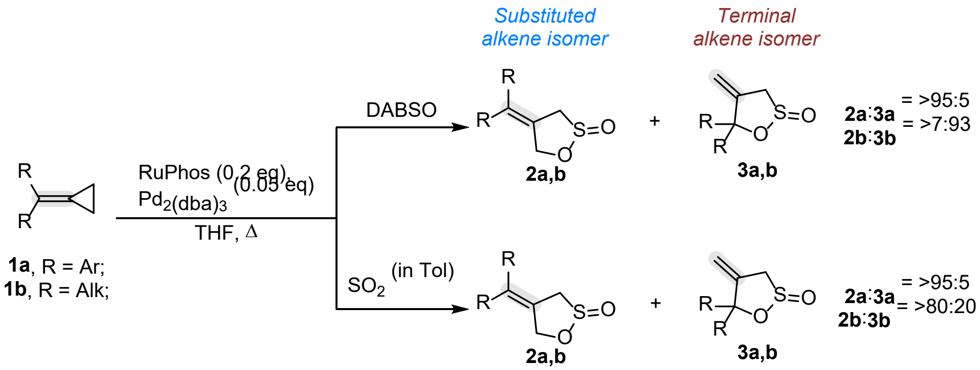

*Figure 1.* Synthesis of isomers sultines 2a,b and 3a,b

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# SYNTHESIS OF FUSED HETEROCYCLES VIA TANDEM 1,2-SILYL SHIFT – FRIEDEL–CRAFTS CYCLIZATION

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Herein we report a new synthetic pathway to fused heterocycles such as chromanes and 1,2,3,4-tetrahydroquinolines. The key synthetic step involves tandem 1,2-silyl shift – Friedel–Crafts cyclization (**Figure 1**). First, propargyl silane **1** undergoes an electrophilic attack, which induces silyl group migration in an *anti*-fashion. This provides a relatively stable allylic cation **2**, which can further react with the internal nucleophile. Previously, our scientific group succesfully applied this concept by affording 5-membered heterocycles **3a**. [1] In this work, we expand our method to the synthesis of larger, 6- and 7-membered heterocycles **3b**, where aromatic system acts as the inner nucleophile via Brønsted acid catalysis.

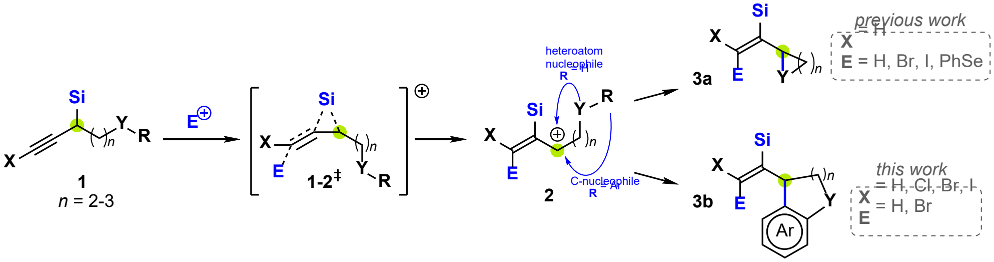

*Figure 1.* Application of 1,2-Silyl Shift in Heterocyclization Reaction: Proposed Mechanism

Additionally, we have optimized the synthesis of functionalized propargyl silanes **1** from commercially available alkynols. This synthesis includes *O*-silylation, retro-Brook rearrangement [2] under Schlosser conditions and modified [3] Mitsunobu reaction with corresponding aryl nucleophiles. In order to increase functionalization of the molecule, terminal alkyne **1** can be easily converted to haloalkyne and employed in same catalytic conditions to yield various fused heterocycles with *Z*-selective alkene side chain.

**Acknowledgements**. The authors thank the Latvian Council of Science Grant No. LZP-2023/1-0576 and Riga Technical University Master Research Grant No. ZM-2024/6 for financial support.

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# SECTION OF
# INSTITUTE OF CHEMICAL PHYSICS

# THERMOELECTRIC AND ELECTROCHEMICAL CHARACTERISATION OF NATURAL POLYMER-BASED HYDROGELS

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With the growing need for sustainable energy solutions, finding efficient ways to convert low-grade waste heat into electricity has become increasingly important. Ionic thermoelectric hydrogels are lightweight, mechanically flexible, and non-toxic materials with great potential in heat-to-electricity conversion. Compared to synthetic polymers, natural biopolymers have multiple advantages, including low cost, wide availability, biodegradability, and excellent mechanical properties, which is beneficial for the fabrication of the hydrogel-based composite materials [1]. This study explores the use of a natural polysacharide for the fabrication of efficient, environment-friendly, ionic thermoelectric material.

In the present work, a nanofluidic platform based on the biopolymer impregnated with $Na^+$ containing aqueous electrolyte in a wide range of concentration was used to implement the ion transport and energy generation by converting thermal energy into electricity. The ion transport within the hydrogel was studied using electrochemical impedance spectroscopy and cyclic voltammetry. The morphology of the polymer matrix was characterized by scanning electron microscopy (SEM). Applying a temperature difference to the system resulted in the increase in output voltage, attributed to thermally driven ion transport.

Based on the results obtained, it was determined how gel density and electrolyte concentration affect the thermopower and capacitance of the fabricated thermoelectric nanofluidic platform, and the optimal parameters have been chosen.

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# AI-INDUCED CHALLENGES

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The development of artificial intelligence (AI) presents significant challenges. Two notable issues are ensuring safety and reassessing the goals and methodologies of science and education. Based on studies of AI operations, we offer an overview of some of these challenges and propose potential solutions.

Reports such as the one to the U.S. Congress [1], the international study on AI [2], and numerous other sources emphasize the possibility of achieving Artificial General Intelligence (AGI) in the coming years. Significant problems have been identified in the operation of autonomous AI systems, including the dangers of AI hallucinations, dishonesty, and the potential loss of control.

The use of AI already poses challenges to science, as understanding and utilizing AI-generated results become increasingly difficult. Soon the human role will be to select and formulate tasks and evaluate outcomes. In line with this projection, the task of the education system is to prepare specialists for effective collaboration with AI. In the longer term, the mission of education and science will be to prepare humanity for life in AI-managed local communities.

Currently, the most important task is to ensure the safe development of AGI, maintaining real control over AI for as long as possible. One solution is a 'bottom-up' approach, which involves embedding human-friendly principles into AI components [chips]. Embedding fundamental prohibitions against harming humanity into chips is feasible by integrating deterministic algorithms with machine learning. One possible method of algorithm notation is the use of mechanical and electromechanical elements, including combinations with quantum computer components.

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# PHOTOTHERMOELECTRIC CHARACTERIZATION OF COPPER OXIDE AND ZINC OXIDE NANOWIRE HETEROSTRUCTURES

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Production of efficient green materials for power generation is a widely discussed topic due to the shrinking reserves of fossil fuels. Along with the increasing scarcity of these resources, burning them produces $CO_2$, which contributes to the greenhouse effect. The need for alternative renewable energy sources will only continue to grow and thus the advancement of materials, which can generate power from sources like sunlight or heat, is imperative. A heterostructured material consisting of copper oxide nanowires and a crystalline zinc oxide layer on top could combine their thermoelectric and photovoltaic properties into a multifunctional green energy source. Copper oxides (CuO and $Cu_2O$) have a high absorption in the infra-red and visible light part of the spectrum, while ZnO has a higher absorption in the ultraviolet and blue light region [1]. By incorporating these oxides into a single heterostructured material, more of the solar radiation spectrum could be utilized via photo- and thermo- related processes and increase the solar energy conversion efficiency.

In this work the proposed heterostructure was fabricated by oxidizing copper foil in air to produce CuO nanowires, and then partially reducing CuO to $Cu_2O$ by annealing in a vacuum [2]. A crystalline layer of zinc was then deposited on the partially reduced copper oxide nanowires via physical vapour deposition and subsequently oxidized in air to produce zinc oxide [3]. A scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscope was used to characterize the morphology and chemical composition of the material. X-ray diffraction analysis was performed to identify the crystalline composition of the material. Photoelectric and thermoelectric measurements were performed in-situ SEM, using a nanomanipulator SmarAct 13D, under illumination from infrared, red, and blue light emitting diodes.

**Acknowledgements**. This work was performed within the Latvian Council of Science FLPP project No. lzp-2022/1-0239 “Multifunctional hybrid metal oxide nanowire arrays for simultaneous green power generation and $CO_2$ reduction”.

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# THERMAL BEHAVIOUR OF BENZANTHRONE AND ITS 3-SUBSTITUTED DERIVATIVES IN AIR

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Benzanthrone (BA) and its derivatives are belonging to the anthrone dye family and in the recent years have gained significant interest due to their luminescent properties [1]. These compounds exhibit important characteristics, such as photostability and fluorescence emission [2]. However, only few studies are dedicated on stability of BA derived dyes; therefore, the thermal stability of the BA and its derivatives is still an open topic, requiring a detailed investigation.

In the present study, the BA and its 3-substituted derivatives with bromo, amino and nitro group are thermally annealed in air, followed by analysis of chemical bonds using Fourier transform infrared (FTIR) spectrometry, as well as characterization of luminescence properties.

The thermal behaviour analysis was performed by applying stepwise annealing in the custom-built thermal annealing system, in the temperature range from 150 up to 300 °C, with the step of 25 °C.

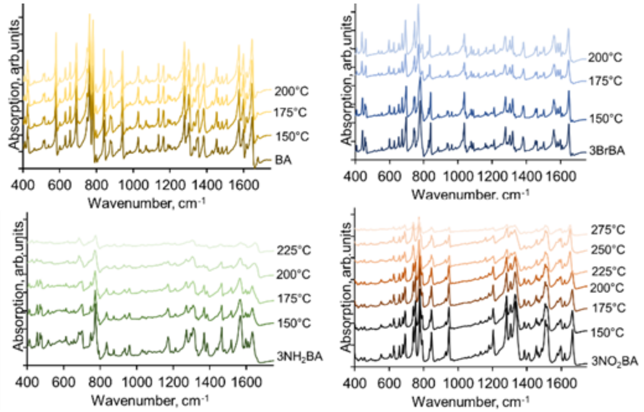

*Figure 1.* FTIR spectra of BA and 3-substituted dyes before and after annealing

During annealing, no structural changes have been observed within the molecules of BA and 3-BrBA up to 200 °C, this corresponds to stable luminescence properties.

Meanwhile, 3-$NH_2$BA and 3-$NO_2$BA derivatives show both changes in chemical bonds and luminescence behaviour.

**Acknowledgements.** This study has been performed within the framework of Latvian Council of Science project No. LZP-2022/1-0436 "Novel fluorescent anthrone-derived functional materials for bioimaging applications".

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# ADVANCED ANODES FOR SUSTAINABLE AQUEOUS RECHARGEABLE BATTERIES

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The demand for sustainable and cost-effective energy storage solutions has led to extensive research into aqueous rechargeable batteries. These batteries have many advantages over lithium-ion systems, including a high natural abundance of materials used for electrodes and environmental safety. However, the use of aqueous metal-based batteries, for example, zinc-based batteries (AZB), is limited by the instability of metal anodes. Traditionally, pure metal foil is used as the anode material due to its simplicity and availability, but it suffers from several drawbacks, including dendritic growth, passivation layers, and hydrogen release, reducing its long-term performance. These issues cause poor metal deposition, higher resistance, and anode degradation over multiple charge-discharge cycles [1].

Nanostructured and nanoporous materials offer new opportunities for stabilizing metal anodes and enhancing their electrochemical properties. Their large surface area and porous structure provide space for dendrites to grow internally, preventing short circuits with the cathode and improving overall battery performance.

The focus of this work is on the development of binder-free advanced metal anodes, synthesized via green chemistry approaches. These electrodes improve charge distribution and regulate metal deposition, effectively decreasing dendrite formation and improving cycling stability. To assess their performance, electrochemical impedance spectroscopy, cyclic voltammetry (CV), and galvanostatic charge-discharge measurements were conducted in various aqueous electrolytes.

The results may demonstrate that advanced anodes enhance the efficiency and sustainability of aqueous batteries. By optimizing electrode and electrolyte structure, it is possible to develop affordable and environmentally friendly energy technologies for safe and sustainable applications.

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# PHOTOVOLTAIC PROPERTIES OF CUO-CU$_2$O-ZNO HETEROSTRUCTURES UTILIZING COPPER FOIL & GRAPHENE AS THE RESPECTIVE ELECTRODES

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The development of potent green materials for solar energy conversion and potentially even gas reduction is crucial for sustainable power generation, especially in light of current climatic and political challenges. By layering copper (I & II) oxide nanowires and zinc oxide in a heterostructure, we produced such a material wherein a broader spectrum of solar radiation can be utilized. CuO and $Cu_2O$ demonstrate strong absorption in the visible and infrared regions, while ZnO effectively absorbs ultraviolet and blue light [1]. Incorporating graphene as a transparent, conductive top electrode and utilizing a copper substrate as the bottom electrode can enhance charge transport and collection, making the heterostructure highly efficient for photovoltaic applications.

In this study, the CuO-$Cu_2O$-ZnO heterostructure was synthesised by oxidizing a copper substrate in air to form CuO nanowires, followed by partial reduction to $Cu_2O$ through vacuum annealing [2]. Then a nanostructured Zn layer was deposited onto the copper nanostructures via physical vapour deposition, followed by its oxidation in air to form ZnO [3]. Finally, a graphene layer, synthesised with chemical vapour deposition, was transferred on top of the heterostructures by a polymer-assisted transfer technique. Morphological and chemical characterization of fabricated heterostructures was performed using scanning electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray diffraction. Photovoltaic measurements were performed using copper as the bottom electrode and graphene as the top electrode. The properties were evaluated using a Keithley 6430 SourceMeter under ambient conditions using illumination from infrared and visible light-emitting diodes.

**Acknowledgements.** This work was performed within the Latvian Council of Science FLPP project No. lzp-2022/1-0239, "Multifunctional hybrid metal oxide nanowire arrays for simultaneous green power generation and $CO_2$ reduction."

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# NAFION MEMBRANE MODIFICATION WITH CARBON NANOTUBES FOR TRITIUM ELECTROCHEMICAL SEPARATION

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Tritium, a radioactive isotope of hydrogen, is expected to be used as fuel in nuclear fusion. Since tritium is primarily obtained as a by-product in nuclear fission reactors with large quantities of lighter hydrogen isotopes, effective isotope separation systems are required for its use as a nuclear fuel.

One of the methods of tritium separation is electrolysis of tritiated water, during which tritium is concentrated in the water phase. In proton exchange membrane water electrolysis, isotope separation can be further enhanced by modifying the used membrane with nanostructures.

In this study Nafion composite membranes with carbon nanotubes (CNTs) were developed and influence of their quantity and type on the electrochemical separation of tritium was evaluated.

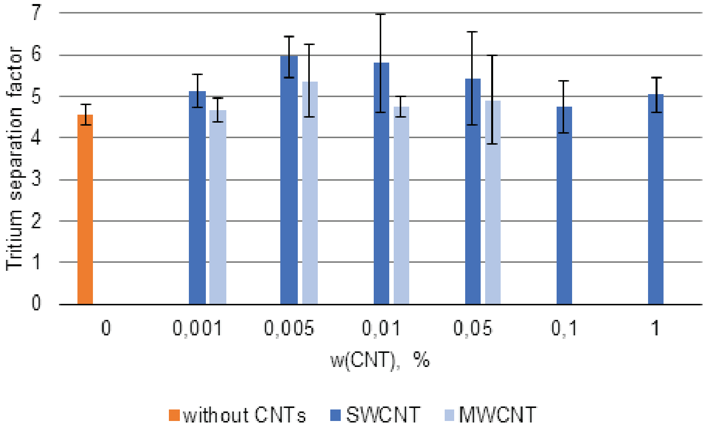

*Figure 1.* Tritium separation factor dependence on CNT mass fraction in membrane

The preliminary results show that CNT composite membranes have an improved tritium separation in comparison to non-modified Nafion, and single-walled carbon nanotube (SWCNT) composites perform better in tritium separation than multi-walled carbon nanotube (MWCNT) composites.

# THE EFFECT OF IONIZING RADIATION ON N,N,N′,N′-TETRA(2-ETHYLHEXYL) DIGLYCOLAMIDE RESIN PERFOMANCE FOR SCANDIUM SEPARATION

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To effectively diagnose and treat malignant tumors, it is possible to use a combination of radioactive isotopes that form a theranostic (therapeutic and diagnostic) pair. Theranostic radioisotopes have a short half-life, requiring their artificial production using nuclear reactors or particle accelerators.

The radioactive isotopes of scandium, $^{43}$Sc, $^{44g/m}$Sc, and $^{47}$Sc, are ideally suited for theranostic purposes. However, for medical applications, purification from various impurities is necessary, which is achieved through physical and chemical methods. [1] One of the most suitable chemical separation methods is solid phase extraction chromatography.

Diglycolamide resins are effective for the selective separation of scandium. Gamma radiation's impact on the chemical structure has been previously reported [2], however, the impact of ionizing radiation on the stability and operational lifespan of these resins remains unclear. In this study, we evaluate irradiated N,N,N',N'-tetra(2-ethylhexyl) diglycolamide (TEHDGA) ion-exchange resin selectivity for scandium, separation efficiency and assess the limits of their potential applications. The TEHDGA resin was irradiated with 10 MeV electrons receiving various absorbed doses.

The results show changes in the chemical structure of TEHDGA and a decreased selectivity towards scandium after irradiation. Separation efficiency for elements such as Ti and V remains unchanged (> 99%), however, Rb separation has decreased.

**Acknowledgements**. The work was carried out within the framework of the Latvian Science Council project No. lzp-2021/1-0539 "A new and efficient approach for the separation and purification of medical radionuclides $^{43}$Sc, $^{44}$Sc and $^{77}$Sc from irradiated metallic targets for the development of radiopharmaceuticals in theranostics".

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# TESTING OF PHOTOELECTROCHEMICAL PERFORMANCE OF ADVANCED HETEROSTRUCTURES

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Batteries that can be directly recharged by light offer a promising solution for balancing the energy surpluses and deficits associated with solar energy. By eliminating the need for external solar panels, they enable more cost-effective off-grid power generation, enhancing both the stability of the electric grid and the quality of life in rural areas.

Photo assisted charging is a process where you take a photo-electrode and implement it into a battery. This method may enhance the batteries energy efficiency and capacity. They work by using high oxidation activity photo-generated holes and high reduction activity photo-generated electrons to reduce the charge and discharge polarization, that stop certain side reaction from occurring in the battery [1]. Photo assisted charging in addition to using aqueous Zn-ion batteries, offers a multitude of advantages, including high safety, abundance of zinc and low cost.

Our group has tested aqueous Zn-ion batteries using different types of materials for the photo-electrode and observed a noticeable improvement in battery capacity and rate of reactions in the battery cell.

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