81th International Scientific
Conference of the
University of Latvia 2023

CHEMISTRY SECTION AND SECTION OF INSTITUTE OF CHEMICAL PHYSICS

BOOK OF ABSTRACTS

UNIVERSITY
OF LATVIA

February–May 2023

81th International Scientific
Conference of the
University of Latvia 2023

CHEMISTRY SECTION AND SECTION OF INSTITUTE OF CHEMICAL PHYSICS

BOOK OF ABSTRACTS

81st International Scientific Conference of the University of Latvia 2023.
Chemistry Section and Section of Institute of Chemical Physics. Book of Abstracts.
Riga: University of Latvia Press. 83 p.

Scientific Committee:
Agris Bērziņš, Kristaps Saršūns, Arturs Vīksna, Agnese Arāja, Artis Kinēns, Edgars Sūna, Artūrs Zariņš, Gunta Kunakova

Editors:
Assoc. prof. Agris Bērziņš
Dr. chem. Artis Kinēns
Prof. Arturs Vīksna
Dr. chem. Artūrs Zariņš

Prepared by the University of Latvia Press

ISBN 978-9934-18-973-9 (PDF)
DOI: https://doi.org/10.22364/iscul.81.cs.ba

CONTENTS

Section of Analytical Chemistry

OCCURRENCE STUDIES OF MYCOTOXINS IN PLANT – BASED BEVERAGES USING LIQUID CHROMATOGRAPHY MASS SPECTROMETRY

Romans Pavļenko[1, 2], Zane Bērziņa[1, 2], Elena Bartkiene[3], Vadims Bartkevičs[1, 2]

[1] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[2] *Institute of Food Safety, Animal Health and Environment "BIOR",*
Lejupes str. 3, Riga, Latvia
[3] *Lithuanian University of Health Sciences, Tilzes g. 18, Kaunas, Lithuania*
E-mail: romans.pavlenko@bior.lv

In recent years there has been a trend towards plant-based alternatives to milk due to medical, ecological and lifestyle reasons. However, raw materials used for the preparation of plant-based drinks could be contaminated with mycotoxins, which are metabolites of moulds that are dangerous to humans. It is necessary to conduct occurrence studies to investigate the prevalence of mycotoxins in this type of food to guarantee food safety.

Within this research, mycotoxins were analysed in plant-based beverages commercially available in markets of the Baltic States. The applied analytical method has been optimised to quantify mycotoxins even at low concentrations [1, 2]6 biogenic amines (BAs. Different sample preparation methods using SPE C18 columns, QuEChERS methodology and PSA clean-up were compared.

61% of all beverages contained mycotoxin at concentrations above the LOQ value and 18 different mycotoxins were detected. The highest occurrence of mycotoxins was found in oat drinks with concentrations of deoxynivalenol and enniatin B1 at 8.6 and 3.2 µg/kg, respectively. The most frequently detected mycotoxins were deoxynivalenol, beauvericin, enniatin B and B1.

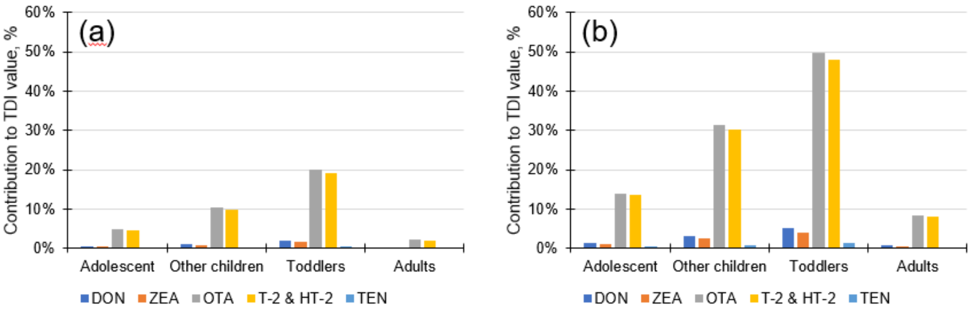


Fig. Mycotoxin contribution to TDI value (a) best-case scenario;
(b) worst-case scenario.

Assuming that a children group replaces cow's milk in their diet entirely with plant-based beverages, the contribution of mycotoxins to the TDI value in case of median consumption would be 10%, 10%, and 1.1% and in case of 95% percentile consumption – 31%, 30% and 3.2% for ochratoxin A, the sum of T-2 and HT-2 toxin, and deoxynivalenol, respectively.

References

[1] Bartkiene, E.; Bartkevics, V.; Pugajeva, I.; Borisova, A.; Zokaityte, E.; Lele, V.; Sakiene, V.; Zavistanaviciute, P.; Klupsaite, D.; Zadeike, D.; Özogul, F.; Juodeikiene, G. *Foods.* **2020**, *9*(5), 614.

[2] Reinholds, I.; Rusko, J.; Pugajeva, I.; Berzina, Z.; Jansons, M.; Kirilina-Gutmane, O.; Tihomirova, K.; Bartkevics, V. *Foods Basel Switz.* **2020**, *9*(1), 93.

IDENTIFICATION AND CHARACTERIZATION OF FRUIT EXTRACTS USING HPLC FINGERPRINTING METHOD

Ance Bārzdiņa, Dace Bandere, Agnese Brangule

Department of Pharmaceutical Chemistry, Riga Stradiņš University,
Konsula str. 21, Riga, Latvia
Baltic Biomaterials Centre of Excellence, Headquarters at Riga Technical University,
Kaļķu str. 1, Riga, Latvia
E-mail: ance.barzdina@rsu.lv

Fruits of various plants have the advantage of having a rich bioactive substance profile and application in both the food and pharmaceutical industries. Therefore, they can potentially be a target of adulterations and falsifications.

The aim of this research was to obtain chromatographic fingerprints of highbush blueberry, bilberry, cranberry, elderberry, and hibiscus extracts, as well as to compare their polyphenolic profile, using HPLC-UV. To analyze different polyphenolic groups (phenolic acids, flavonoids, and anthocyanins) chromatographic fingerprints were obtained at 280 nm, 360 nm, and 520 nm. Principal component analysis, hierarchical cluster analysis, as well as ANOVA test was used to determine if this method can be used to differentiate between these fruits. Statistical analysis was performed on Spectragryph 1.2.15., SpecAlign 2.4.1, Origin 10, and SIMCA 17 software.

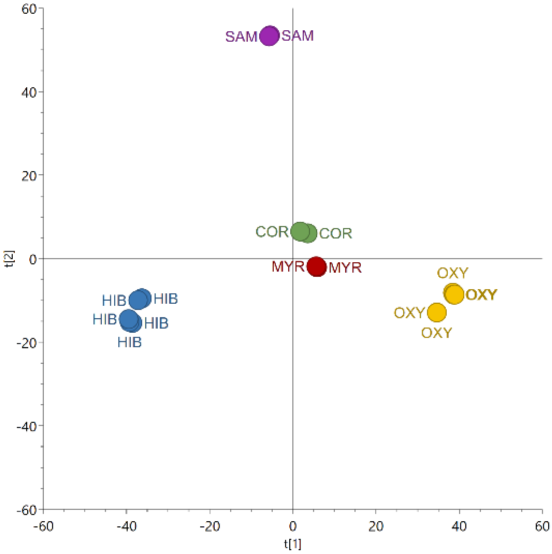


Fig. PCA clusters of fruit extracts detected at 360 nm.
(OXY– cranberry extracts, MYR – bilberry extracts, COR – blueberry extracts, SAM – elderberry extracts, HIB – hibiscus extracts).

The results show significant differences between extracts of analyzed fruits at all 3 wavelengths. It was determined that the biggest phytochemical difference can be seen between cranberry and elderberry extracts. A correlation with the phylogenetic tree can be seen at 520 nm, with all genus *Vaccinium* fruits grouped in one tight cluster while hibiscus and elderberry extracts are in separate clusters. Although bilberry and blueberry extracts have a similar look and profile, they can be identified using chromatographic fingerprints at 280 nm.

The developed chromatographic method can be used to differentiate between otherwise similarly looking fruit extracts proving potential future application in the fight against herbal material adulterations and falsifications.

Acknowledgements. The authors acknowledge financial support from the European Union's Horizon 2020 research and innovation programme under the grant agreement No. 857287 (BBCE – Baltic Biomaterials Centre of Excellence)

EVALUATION OF HONEY FLORAL ORIGINS USING VOLATILE ORGANIC COMPOUND COMPOSITION DETERMINED BY GAS CHROMATOGRAPHY–MASS SPECTROMETRY

Krišs Dāvids Labsvārds[1, 2], Ingus Pērkons[2], Una Briža[1], Arturs Vīksna[1]

[1] Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia
[2] Institute of Food Safety, Animal Health and Environment "BIOR",
Lejupes str. 3, Riga, Latvia
E-mail: kriss_davids.labsvards@lu.lv

There is close competition between honey producers and having a monofloral honey is a great way to stand out in honey market. Besides collection of monofloral honey, another difficult task is confirmation of monofloral botanical origins. Nowadays major method of confirmation of monofloral honey is melissopalynology, which have several drawbacks. This suggests the necessity of alternative confirmation methods, for example modern instrumental analysis. To plants, the volatile organic compounds (VOCs) help to attract bees to collect nectar. Several studies have confirmed that there is a link between VOCs composition and botanical origins [1]. The gas chromatography–mass spectrometry (GC-MS) was proposed as eligible alternative for honey botanical origins evaluation.

In the research 30 monofloral honey samples of different floral origins (buckwheat, clover, heather, linden, rapeseed, willow) were analysed by GC-MS. Untargeted screening was performed, and mass spectra were obtained in full scan mode (20–250 m/z). The VOCs were identified by using National Institute of Standards and Technology (NIST) database. Sample botanical origins were confirmed by melissopalynology analysis and expressed as pollen percentage to help evaluate the GC-MS results.

The preliminary results show that 18 different VOCs have a potential to be used as marker compounds to distinguish floral origins of honey. GC-MS studies show that buckwheat, heather and linden honeys can be distinguished from other floral types of honey. The best results of discrimination were obtained with phenylacetic acid derivatives as selective markers for heather honey, which can be supported by previous studies on NMR [2]. In case of buckwheat honey the combination of furfural and isovaleric acid could be used for discrimination. Linden honey showed least variety of VOCs which can be useful for botanical origins evaluation using modern instrumental analysis. Current results do not show significant differences in VOC composition for clover, rapeseed and willow monofloral honeys.

References

[1] Karabagias, I.K.; Karabagias, V.K.; Nayik, G.A.; Gatzias, I.; Badeka, A.V. *LWT.* **2022**, *154*, 112588.

[2] Labsvards, K.D.; Rudovica, V.; Kluga, R.; Rusko, J.; Busa, L.; Bertins, M.; Eglite, I.; Naumenko, J.; Salajeva, M.; Viksna, A. *Foods.* **2022**, *11*, 42.

Acknowledgements. "Strengthening of the capacity of doctoral studies at the University of Latvia within the framework of the new doctoral model", identification No. 8.2.2.0/20/I/006.

IDENTIFICATION OF BALLPOINT PEN INK COMPONENTS AND ITS AGING ESTIMATION AFTER DOCUMENT WERE STORED IN THE DARK

Megija Neimane[1, 2], Vita Rudoviča[1], Vitālijs Freidenfelds[2], Antons Podjava[1]

[1] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[2] *State Forensic Science Bureau Republic of Latvia, Invalīdu str. 1, Riga, Latvia*
E-mail: megija.neimane@lu.lv

The most relevant and one of the most difficult issues that questioned document experts solve is related to the detection of document dating. Backdating documents are used in committing financial crimes, fraud, smuggling etc. In order to investigate whether the particular documents are signed with a backdated date, or other amendments were made with different pens, an analysis of the chemical composition of the ink is carried out [1, 2].

After the ink is applied to the surface of the paper, it begins to age. To detect the age of the ink, the most frequently used method is chromatographic methods – gas and high-performance liquid chromatography (GC and HPLC). Liquid chromatography determines the chemical composition of dyes and solvents using ratio of signal areas and ink age [3].

In the research, 13 blue and 9 black ballpoint pen inks, which were purchased on different brands, were applied to document paper drawing straight lines and analysed after stored in the office drawer in darkness. The dyes in the ballpoint pen inks were determined using high performance liquid chromatography-mass spectrometry, while the solvents were determined using gas chromatography-mass spectrometry. The aging curves of ink components constructed using obtained data by HPLC with a fluorescence and diode array detector.

Obtained results show that in the inks of both colours contain the solvent – phenoxyethanol, the dyes – tetramethyl violet, pentamethyl violet and crystal violet, but in the blue ink are also basic blue 26 or brilliant blue FCF, while the black ink also contains methanyl yellow. It was found that aging process of ballpoint pen inks when documents stored in the dark is relatively fast during the first month and then aging continues at a steady rate.

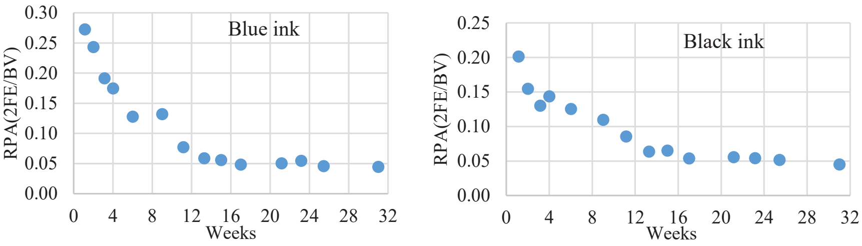


Fig. Natural aging of blue and black ballpoint pen ink after storage in the dark (relative peak area (RPA) – phenoxyethanol (2FE) to basic violet (BV) dyes in 8 month time).

References

[1] Weyermann, C.; Kirsch, D.; Costa-Vera, C.; Spengler, B. *Forensic Sci. Int.* **2007**, *168*, 119–127.

[2] Gorai, A.; Pal, R.; Gupta, P. *IJCNN*. **2016**, 4512–4517.

[3] Izzharif Abdul Halim, M.; Saim, N.; Osman, R.; Jasmani, H.; Nadhirah Zainal Abidin, N. *Malaysian J. Anal. Sci.* **2013**, *17*, 230–235.

OCCURRENCE OF ANTIBIOTICS AND ANTIVIRAL DRUGS IN WASTEWATER FROM 14 LATVIAN CITIES

Anna Skrastiņa, Deniss Fedorenko, Arvis Prikulis, Vadims Bartkevičs
Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia
Institute of Food Safety, Animal Health and Environment "BIOR", Lejupes str. 3, Riga, Latvia
E-mail: anna.skrastina@bior.lv

Infectious diseases are recognized as one of the most important threats to public health. The ability to rapidly monitor the spread of diseases is essential for prevention and control. Wastewater-based epidemiology (WBE) is a new epidemiology tool that can act as a complementary instrument to current infectious disease surveillance systems and act as an early warning system for infectious disease outbreaks [1].

In this study, 10 antibiotics and 4 antiviral agents were analysed in 100 wastewater samples from 14 Latvian cities sampled from august to November of 2022. Macrolide antibiotics, sulfamethoxazole, abacavir and acyclovir were found in all samples. The highest consumption of antibiotics is determined for macrolide antibiotics, followed by fluoroquinolones and sulfamethoxazole and trimethoprim, which corresponds to the most consumed groups of antibiotics in Latvia estimated by the European Center for Disease Prevention and Control. The consumption of the drugs examined in the study increases noticeably in September but is lower in the following autumn months. This information coincides with the monthly turnover of medicines in 2022. The study demonstrates the applicability of the approach based on instrumental WW analysis to trace changes in antibiotics and antiviral drug consumption patterns.

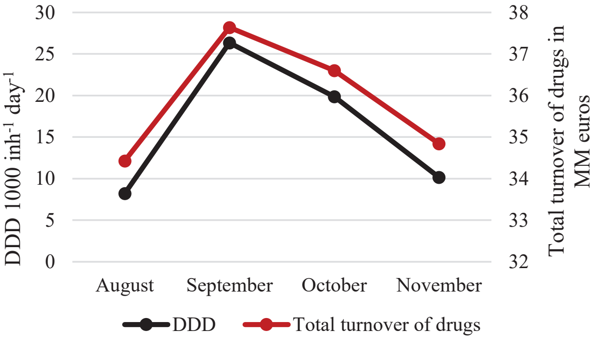


Fig. The total calculated consumption of the studied drugs and the total turnover of the drugs in 2022.

Reference

[1] Sims, N.; Kasprzyk-Hordern, B. *Environment International.* **2020**, *139*, 105689.

Acknowledgements. This research was funded by project No. VPP-EM-BIOMEDICĪNA-2022/1-0001.

THE APPLICABILITY OF THE DILUTE-AND-SHOOT METHODOLOGY FOR THE DETERMINATION OF SEVERAL BIOMARKERS AND PHARMACEUTICALS IN WASTEWATER USING NANOFLOW LIQUID CHROMATOGRAPHY – ORBITRAP MASS SPECTROMETRY

Deniss Fedorenko[1, 2], Antons Podjava[1], Arvis Prikulis[1, 2], Vadims Bartkevičs[1, 2]

[1] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[2] *Institute of Food Safety, Animal Health and Environment "BIOR", Lejupes str. 3, Riga, Latvia*
E-mail: deniss.fedorenko@bior.lv

The content of endogenous chemical compounds in wastewater (WW) samples could provide a comprehensive insight into the well-being and lifestyle habits of a population. The principles for describing changes in concentrations of endogenous compounds and pharmaceuticals in environmental samples, such as WW, form a basis of wastewater-based epidemiology (WBE) [1].

A novel method for quantitative analysis of population and lifestyle biomarkers, as well as several pharmaceutical compounds in WW has been developed employing nanoflow liquid chromatography (nano-LC) with Orbitrap mass spectrometry. The method was applied to the analysis of untreated WW samples from the WW treatment plants in several cities and towns of Latvia. The new nano-LC method demonstrated low matrix effects, good sensitivity, low injection volume and solvent consumption, as well as the ability to analyse diverse polar and ionic analytes within one run using a single reversed-phase nano-LC column.

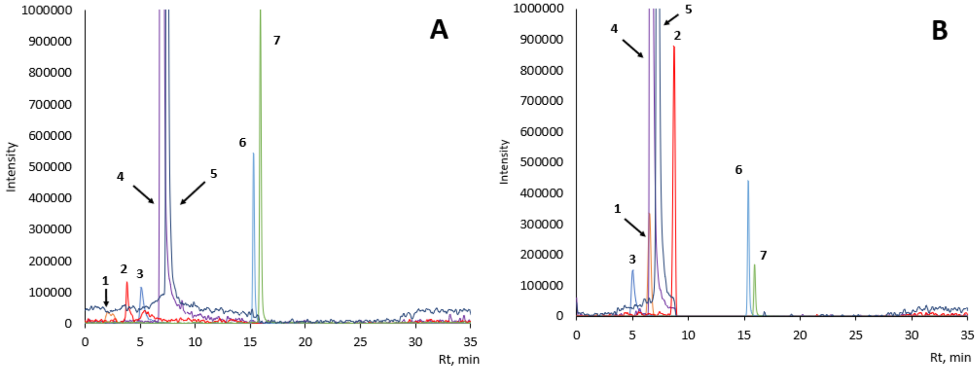


Fig. Chromatograms of the analysed pharmaceutical compounds and biomarkers (1 – ethyl sulphate, 2 – 5-HIAA, 3 – gabapentin, 4 – cotinine, 5 – caffeine, 6 – diclofenac, 7 – ibuprofen) without addition of TBAB reagent (A), with the addition of optimal concentration of 11 mM of TBAB (B).

The study demonstrated that the use of in-sample addition of ion-pair reagent improves the retention of highly polar compounds in nano-LC and this approach combined with a rapid sample preparation procedure based on the dilute-and-shoot methodology can be very efficient for the quantitative analysis of pharmaceuticals and biomarkers in WW.

Reference

[1] Tomsone, L.E.; Perkons, I.; Sukajeva, V.; Neilands, R.; Kokina, K.; Bartkevics, V.; Pugajeva, I. *Water Research*. **2022**, *221*, 118800.

Acknowledgements. This research is funded by the Ministry of Economics, project "State research project in the field of biomedicine, medical technologies and pharmacy", project No. VPP-EM-BIOMEDICĪNA-2022/1-0001.

METHOD DEVELOPEMENT FOR THE DETERMINATION OF PER- AND POLYFLUORINATED COMPOUNDS IN FOOD

Elīna Pasečnaja[1, 2], **Dzintars Začs**[2]

[1] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[2] *Institute of Food Safety, Animal Health and Environment “BIOR”, Lejupes str. 3, Riga, Latvia*
E-mail: elina.pasecnaja@bior.lv

Per- and polyfluorinated alkyl substances (PFASs) comprise a large group of anthropogenic chemicals which are ubiquitous environmental contaminants. In 2020 European Food Safety Authority (EFSA) concluded that perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorohexanesulfonic acid (PFHxS) and perfluorooctanesulfonic acid (PFOS) can cause developmental effects and may have adverse effects on serum cholesterol, the liver, the immune system, and birth weight. EFSA considered the effects of PFAS on the immune system as the most critical and established a group tolerable weekly intake (TWI) of 4.4 ng kg^{-1} b.w.$^{-1}$ per week for the sum of these four PFASs. Recently, the European Commission has established maximum levels for PFASs in certain foods, focusing on limits for priority four PFASs. Therefore, more sensitive analytical methods or improved analytical protocols should be applied to ensure the analysis of PFASs at occurrence levels that comply with the newly established EFSA TWI of 4.4 ng kg^{-1} b.w. [1].

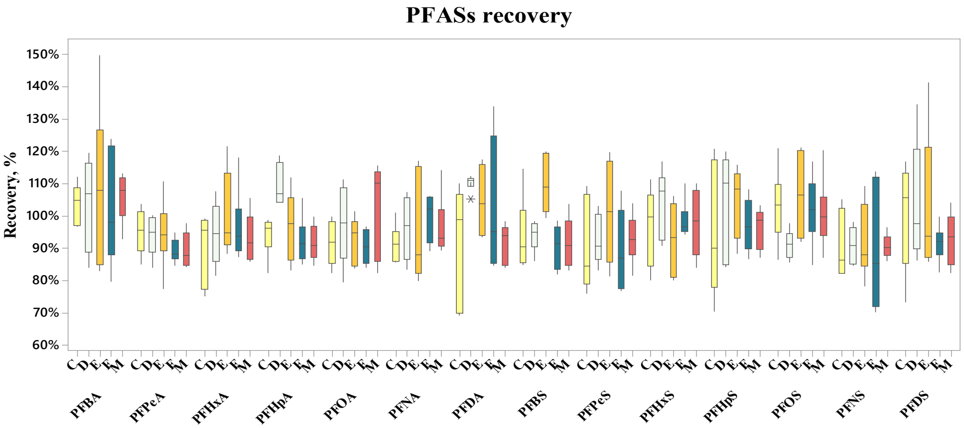


Fig. PFASs C4-C10 recovery in test matrices.

An improved analytical methodology allows to determine 14 PFASs along with four priority components using HPLC-Orbitrap-MS. Based on Guidance document the following analytical performance criteria were verified – analytical recovery, linearity, limit of quantification (LOQ), precision and trueness, and estimation of measurement uncertainty (MU). Analytical recovery for four priority PFASs were in range 80–120%, while for short and long chain compounds recovery is in range 70–135%. The linearity over the concentration range of 0.5–500 pg µL–1 was observed for selected PFAS with correlation coefficients ≥0.995, while trueness and precision were in range 3–7% and 1–8% respectively. LOQ values for PFASs were 0,01 µg kg^{-1} w.w. except for long chain representatives which LOQ values were 0,50 µg kg^{-1} w.w. The observed performance characteristics of the method demonstrated that it fulfils specified requirements from the Guidance Document on Analytical Parameters for the Determination of Per- and Polyfluoroalkyl Substances (PFAS) in Food and Feed [1].

Reference

[1] European Union Reference Laboratory for halogenated POPs in feed and food. Guidance Document on Analytical Parameters for the Determination of Per- and Polyfluoroalkyl Substances (PFAS) in Food and Feed. **2022.**

DETECTION OF MYCOTOXINS AND PYRROLIZIDINE ALKALOIDS IN A WIDE VARIETY OF NUTRITIONAL SUPPLEMENTS USING HPLC-MS/MS

Zane Bērziņa[1, 2], **Romans Pavļenko**[2], **Vadims Bartkevičs**[1, 2]

[1] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[2] *Institute of Food Safety, Animal Health and Environment "BIOR", Lejupes str. 3, Riga, Latvia*
E-mail: zane.berzina@bior.lv

Plant-based nutritional supplements are considered a natural means of enriching the everyday diet, but they could be also a source of various food contaminants such as mycotoxins [1] and pyrrolizidine alkaloids [2]. Both groups of food contaminants include chemical compounds that can significantly affect the health of the consumer.

In this context, the aim of the present study was to perform a multi mycotoxin and pyrrolizidine alkaloid analysis (81 compounds in total) in 25 tablet samples of herbal dietary supplements containing at least one herbal ingredient, and 20 herbal infused syrup samples. The sample preparation was performed by the QuEChERS method and the determination by high performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS).

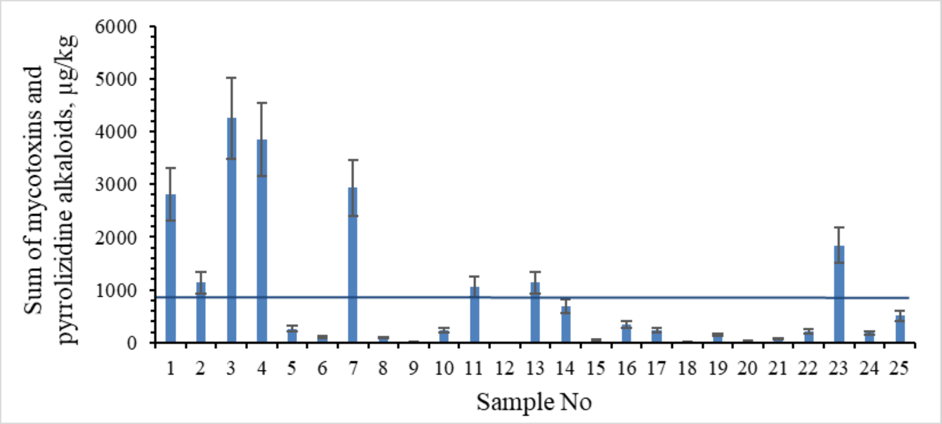


Fig. The sum of concentrations of mycotoxins and pyrrolizidine alkaloids in tablet samples of herbal dietary supplements.

Herbal infused syrup samples contained minimal amounts of investigated contaminants, while concentrations found in powdered and tablet form nutritional supplements reached up to 4.25 mg/kg, but on average was 0.83 mg/kg. The number of compounds found per sample varied from 1 to 29, with a median of 14 compounds per sample. Although the obtained results are lower than previously published [1], the daily intake of mycotoxins and pyrrolizidine alkaloids might significantly increase with the regular use of such nutritional supplements.

References

[1] Veprikova, Z.; Zachariasova, M.; Dzuman, Z.; Zachariasova, A.; Fenclova, M.; Slavikova, P.; Hajslova, J. *J. Agric. Food Chem.* **2015**, *63*(29), 6633–6643.

[2] Jansons, M.; Fedorenko, D.; Pavlenko, R.; Berzina, Z.; Bartkevics, V. *J. Chrom. A.* **2022**, *1676*, 463269.

Acknowledgement. "Strengthening of the capacity of doctoral studies at the University of Latvia within the framework of the new doctoral model", identification No. 8.2.2.0/20/I/006.

THE ANALYSIS OF ELECTROCHEMICAL PERFORMANCE OF NANOSTRUCTURED BI_2SE_3 THIN FILMS AS ANODES FOR AQUEOUS RECHARGEABLE LITHIUM-ION BATTERIES

Vitālijs Lazarenko[1, 2], Yelyzaveta Rublova[1], Raimonds Meija[1],
Jana Andžāne[1], Arturs Vīksna[2], Donāts Erts[1, 2]

[1] Institute of Chemical Physics, University of Latvia, Raiņa blvd. 19, Riga, Latvia
[2] Faculty of Chemistry, University of Latvia, Raiņa blvd. 19, Riga, Latvia
E-mail: vitalijs.lazarenko@lu.lv

In the last 20 years, lithium-ion batteries (LIBs) have become the primary choice in the development of various types of portable devices (laptops, mobile phones, etc.). Such a drastic development growth of the technology industry has created a huge demand for new alternative ways of energy storage devices (EES) with enchantment performance. One of the perspectives of EES is aqueous rechargeable lithium-ion batteries (ARLIBs) which have attracted attention as cheaper and more environmentally friendly battery systems. The use of lithium-aqueous electrolytes ($LiNO_3$, LiCl, etc.) reduces the risk of flammability and explosiveness. In the meantime, significant progress in ARLIBs has been achieved in the development of different cathode materials, however, the development of anodes is still the main drawback (e.g., significant capacity fading during the charge/discharge processes). Bi_2Se_3 is a unique material that has already shown its perspective use as an anode for LIBs and likely can be a promising candidate for ARLIBs.

The aim of this research was to investigate the electrochemical performance of nanostructured Bi_2Se_3 thin films as anodes for ARLIBs. For the investigation was formed two different layers on the Bi_2Se_3 surface (SEI and Bi_2O_3 layer) by applying different potential ranges. As the electrolyte was used 5 M $LiNO_3$ solution. The Bi_2Se_3 thin films were synthesized using a physical vapour deposition method. Different electrochemical measurement techniques were applied (cycling voltammetry, galvanostatic charge/discharge, electrochemical impedance spectroscopy) to investigate the electrochemical properties and performance. The chemical composition and surface morphology was investigated by using a scanning electron microscope equipped with energy-dispersive X-ray, X-ray diffraction analysis, and X-ray photoelectron spectroscopy.

The results of this work demonstrated the possible perspectives of nanostructured Bi_2Se_3 thin films as anodes for ARLIBs. Bi_2Se_3 thin films with a formed SEI layer demonstrated the best electrochemical performance than with the Bi_2O_3 layer. Such a fact can be explained by the great stability of the SEI layer which ensures high Li^+ transportation, rapid pre-treatment, high charge/discharge capacities, and high Coulombic efficiency [1].

Reference

[1] Lazarenko, V.; Rublova, Y.; Meija, R.; Andzane, J.; Voikiva, V.; Kons, A.; Sarakovskis, A.; Viksna, A.; Erts, D. *Batteries*. **2022**, *8*, 144.

Acknowledgements. This research was funded by the European Regional Development Fund Project (ERDF) No. 1.1.1.1/19/A/139. V.L. acknowledges the support of "Strengthening of the capacity of doctoral studies at the University of Latvia within the framework of the new doctoral model", identification No. 8.2.2.0/20/I/006.

DEVELOPMENT AND EVALUATION OF IN-HOUSE MATRIX-MATCHED STANDARDS FOR LA-ICP-MS ANALYSIS OF TREE RINGS IN DENDROCHEMISTRY RESEARCH

Māris Bērtiņš[1], Paarn Paiste[2], Ligita Ostrovska[1], Armands Ozols[1], Vita Rudoviča[1], Kalle Kirsimae[2], Māris Kļaviņš[3], Arturs Vīksna[1]

[1] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[2] *Faculty of Science and Technology, Department of Geology,*
Institute of Ecology and Earth Sciences, University of Tartu,
Ravila 14A, 50411 Tartu, Estonia
[3] *Faculty of Geography and Earth Sciences, University of Latvia, Jelgavas str. 1, Riga, Latvia*
E-mail: maris.bertins@lu.lv

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is a highly suitable method for the analysis tree rings due to its high spatial resolution, wide range of measurable elements and isotopes, and minimal sample preparation requirements. However, quantifying the data obtained by this technique can be challenging. The calibration of LA-ICP-MS is typically performed using silicate standard reference materials, which have a glass matrix and are not suitable for external calibration of elements in tree rings due to the differences in the matrix and the lack of carbon as an internal standard for wood samples. Therefore, in-house matrix-matched standards are necessary for accurate quantification of element concentrations in tree rings using LA-ICP-MS.

In this study, we aimed to prepare and compare various in-house matrix-matched standards for quantifying element concentrations in tree rings. We used cellulose, the primary constituent of wood, as the base material for the preparation of reference materials. We doped three different microcrystalline cellulose powders (50 µm, 20 µm, and nanosized, Sigma-Aldrich) with various elements and pressed them into 10 mm pellets. The content of the elements in the prepared cellulose pellets was confirmed using acid digestion and ICP-MS analysis. Additionally, in-house standards were compared to certified reference materials, isuch as IAEA 336 (lichen), IAEA 413 (algae), IAEA 392 (algae), and BRC 692 (white cabbage).

The results showed that the homogeneity of the prepared standards was influenced by the particle size of the material used for pellet preparation. Furthermore, it was found that the IAEA 392 (algae) powder could be directly pressed into a pellet without additional milling to produce a sufficiently homogeneous material for use as a matrix-matched standard. These findings can contribute to improving the accuracy of LA-ICP-MS analysis of tree rings and promote further research in dendrochemistry.

In summary, the preparation of in-house matrix-matched standards is necessary for accurate quantification of element concentrations in tree rings using LA-ICP-MS. Using cellulose as the base material for reference materials can facilitate the preparation of matrix-matched standards. The results highlight the importance of careful consideration of particle size and matrix when preparing in-house standards and offer a viable alternative to certified reference materials.

Acknowledgement. Research is supported by “Strengthening the doctoral capacity of the University of Latvia within the framework of the new doctoral model” with project identification No. 8.2.2.0/20/I/006, LU registration No. ESS2021/434, co-financed by the European Social Fund.

ENHANCING TRACE ELEMENT DETECTION LIMITS USING ICP-MS IN O_2 REACTION MODE: IMPLICATIONS FOR ENVIRONMENTAL MONITORING AND MATERIAL SCIENCE

Irina Shtangeeva[1], Māris Bērtiņš[2], Linda Ansone-Bērtiņa[3], Agnese Brangule[4], Māris Kļaviņš[3], Arturs Vīksna[2]

[1] *Institute of Earth Sciences, St. Petersburg University,*
Universitetskaya nab. 7/9, St. Petersburg, Russia
[2] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[3] *Faculty of Geography and Earth Sciences, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[4] *Department of Pharmaceutical Chemistry, Riga Stradiņš University,*
Dzirciema str. 16, Riga, Latvia
E-mail: maris.bertins@lu.lv

The literature on trace elements in the environment is vast, and while fewer than twenty elements have been recognized as essential nutrients, there are numerous publications on heavy metals. However, it is reasonable to assume that all chemical elements play a role in specific biochemical processes, unfortunately, a lack of quality analytical techniques limits information on the toxicity or importance of these elements. In recent years, determining very low concentrations of elements has become increasingly important in various fields, including environmental monitoring, pharmaceuticals, food, and material science. Trace elements such as Co, Se, Mo, Cr, W, and also rare earth elements have been of great interest due to their impact on human health and the environment.

To determine trace amounts of elements in different matrices, analytical chemists have used various techniques. Among them, inductively coupled plasma mass spectrometry (ICP-MS) is one of the most powerful techniques available today. ICP-MS is highly sensitive and can detect trace elements at concentrations as low as parts per trillion (ppt). However, detecting these trace elements using ICP-MS is not always straightforward, and various challenges arise, such as matrix interferences, spectral interferences, and memory effects.

In this study, we used Agilent QQQ 8900 ICP-MS equipment in different reaction gas modes, to determine very low concentrations of trace elements.

Our results showed that most of the elements studied can be directly determined in concentration levels down to 10 ng/L using ICP-MS. However, for some elements, such as Si, Ti, Mo, and W, the use of an O_2 reaction cell significantly decreased the detection limits. For example, the detection limits for Si, Ti, Mo, and W were 26, 13, 5, and 4 ng/L, respectively, using the O_2 reaction cell.

In conclusion, determining trace amounts of elements is essential for various applications, and ICP-MS is a powerful technique for achieving this goal. Our study demonstrated that the Agilent QQQ 8900 ICP-MS equipment in MS/MS mode with O_2 reaction gas can significantly enhance the detection limits of elements like Si, Ti, Mo, and W. These results have significant implications for environmental monitoring, material science, and other applications where trace element detection is critical.

Acknowledgement. Research is supported by "Strengthening the doctoral capacity of the University of Latvia within the framework of the new doctoral model" with project identification No. 8.2.2.0/20/I/006, LU registration No. ESS2021/434, co-financed by the European Social Fund.

THE IMPACT OF ARGININE PHOSPHATE-CONTAINING FERTILIZER ON GROWTH AND NUTRIENT CONTENT OF SCOTS PINE AND NORWAY SPRUCE IN LATVIAN FORESTS

Jana Svinska[1], Māris Bērtiņš[1], Lauma Buša[1], Sindija Žīgure[2], Dagnija Lazdiņa[2], Kārlis Dūmiņš[2], Māris Kļaviņš[3], Arturs Vīksna[1]

[1] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[2] *Latvian State Forest Research Institute "Silava", Rigas str. 111, Salaspils, Latvia*
[3] *Faculty of Geography and Earth Sciences, University of Latvia, Jelgavas str. 1, Riga, Latvia*
E-mail: maris.bertins@lu.lv

Latvia's forested territory accounts for over half of its total area, with around 3.4 million hectares of forests covering the land. This area is constantly expanding due to afforestation efforts in abandoned agricultural and former mining areas, as well as natural forest growth. Forest soil fertilization is an essential technique used to improve the growth and competitiveness of seedlings in forest environments. The addition of essential nutrient elements such as nitrogen is a commonly employed fertilization method.

This study involved four research sites comprising Vacciniosa mel. dry and drained mineral soil and Myrtillosa dry and drained mineral soil type forests. The impact of arginine phosphate-containing fertilizer on the growth of Scots pine (Pinus sylvestris L.) and Norway spruce (Picea abies (L.) H. Karst) was investigated by analyzing isotope ratio and elemental content in needle, branch, root, and soil samples from both fertilized and control plots.

To determine the effect of soil improvers and fertilizers on plant growth, isotopically marked nitrogen fertilizer was used in combination with light-stable isotope ratio mass spectrometry (IRMS) and inductively coupled plasma mass spectrometry (ICP-MS, Agilent 8900 ICPMS QQQ). The data obtained were evaluated and statistically analyzed using the Chemometric Agile Tool (CAT) and statistical software program R.

The primary objective of the study was to evaluate changes in isotopic and elemental content in Scots pine and Norway spruce as a result of the application of arginine phosphate-containing fertilizer in the experimental plots. Following fertilization with arginine phosphate-containing fertilizer, an increase in the mass fraction of nitrogen was observed in spruce needles, and there was a decrease in the nitrogen isotope ratio. However, no significant trend was observed in pine seedlings, leading to the conclusion that arginine phosphate was not the primary source of nitrogen in pine needles. In the second growing season, changes were still evident in the spruce samples, although no significant differences in nitrogen isotope ratio were observed between fertilized and unfertilized pine samples.

In conclusion, the study showed that the use of arginine phosphate-containing fertilizer can have a positive impact on the growth of forest plants. However, the effectiveness of the fertilizer may differ depending on the plant species, as demonstrated by the differences observed between the Scots pine and Norway spruce samples. This research contributes to the development of sustainable forest management practices and can help to improve the competitiveness and growth of forest plants.

Acknowledgements. Research is supported by the Latvian State forest projects No. 3.5.5-5.1-000z-101-16-31 and No. 5-5.9.1_007n_101_21_77 and “Strengthening the doctoral capacity of the University of Latvia within the framework of the new doctoral model” with project identification No. 8.2.2.0/20/I/006, LU registration No. ESS2021/434, co-financed by the European Social Fund.

EXTRACTION OF FERULIC ACID FROM ORGANICALLY AND CONVENTIONALLY GROWN WHEAT GRAIN

Elīza Grence[1], Lauma Buša[1], Solveiga Maļecka[2], Kristīne Meile[3], Arturs Vīksna[1]

[1] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[2] *Institute of Agricultural Resources and Economics, Stende Research Centre, "Dižzemes", Dižstende, Lībagi parish, Talsi district, Latvia*
[3] *Latvian State Institute of Wood Chemistry, Dzērbenes str. 27, Riga, Latvia*
E-mail: lauma.busa@lu.lv

Ferulic acid (*(E)-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoic acid*) represents the most common phenolic acid located in wheat bran [1], therefore it is a potential marker to distinguish between conventionally and organically grown wheat grain.

In the research, ferulic acid from organically and conventionally grown wheat grains was extracted and analysed using HPLC. The grain samples were obtained from Institute of Agricultural Resources and Economics, Stende Research Centre. A total of four organically (BIO) and four conventionally (CON) grown wheat grain samples were analyzed. Two different extraction methods were used. **Method 1** used 20 mL of 2 M NaOH, 10 mM EDTA and 1% ascorbic acid mixture. The extraction was carried out at 45 °C for 30 minutes. **Method 2** was carried out at room temperature for 3 hours. For extraction 10 mL of 80% ethanol solution and 5 mL of 6 M NaOH solution were used. The results of mass concentration of ferulic acid in wheat grains are summarized in Fig.

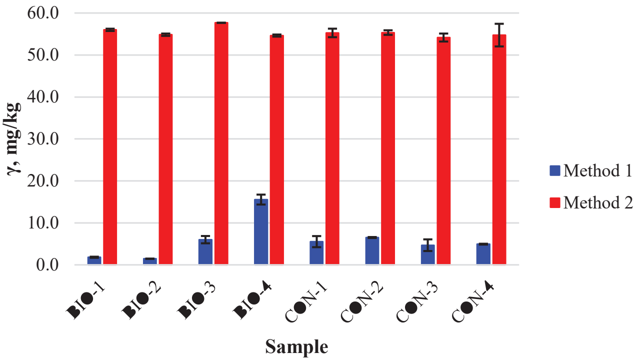


Fig. Mass concentration of extracted ferulic acid in wheat grains.

The preliminary results show that the difference between mass concentration of extracted ferulic acid from organically and conventionally grown wheat grains is not statistically significant ($p > 0.1$). However, the amount of extracted ferulic acid varies greatly, depending on the extraction method used. Higher amounts of ferulic acid can be extracted using more concentrated NaOH solution over longer period of time at room temperature.

Reference

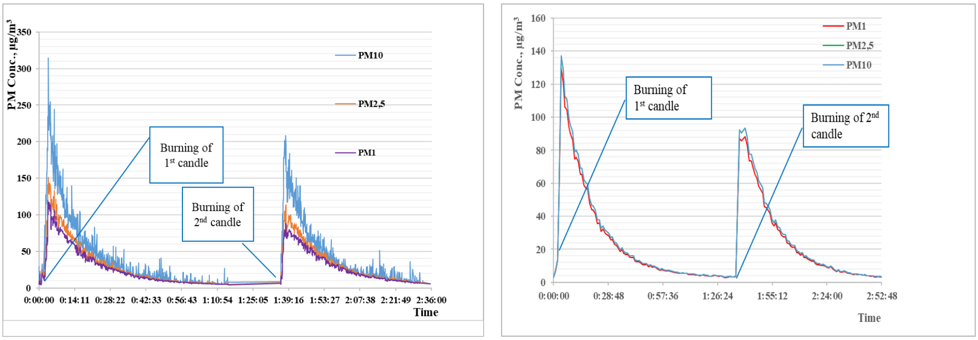
[1] Horvat, D.; Šimić, G.; Drezner, G.; Lalić, A.; Ledenčan, T.; Tucak, M.; Plavšić, H.; Andrić, L.; Zdunić, Z. *Antioxidants*. **2020**, *9*(6), 527–538.

CHARACTERIZATION OF CONCENTRATION CHANGES OF AEROSOL PARTICLES IN INDOOR AIR DURING THE BURNING OF FOUNTAIN CANDLES

Laima Pļaveniece, Agnese Arāja, Māris Bērtiņš, Gunita Celma
Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia
E-mail: laima.plaveniece@gmail.com

Residential indoor air quality remains considerable concerns and indoor microenvironment air contamination is one of the main current environmental health risks, since it has been reported that people in industrialized countries spend an average 90% of their time in enclosed microenvironments [1]. Secondly, air pollutants frequently are at higher levels indoors than in outdoor environment in accordance with the World Health Organization (WHO) [2]. It should be noted that indoor air quality is affected not only by outdoor air pollutant concentrations, but also by human activities performed indoors such as cooking, cleaning, smoking and candle burning. Burning of candles, magic candles, incense, and pyrotechnics such as fountain candles brings joy during celebrations. But most people never even thought about the smoke, particulate matter produced and the pollution that occurs and remains in indoor air after such activities.

In the current work, simulating studies of burning fountain candles were performed for quantitative and qualitative analysis of obtained particulate matter, more precisely – mass concentrations of PM_{10}, $PM_{2.5}$ and PM_1, and number concentrations of obtained ultra fine particles were determined, using the measuring device – the Grimm environmental aerosol spectrometer EDM365 and particulate matter sensors Pod2 and SPS30.



A

B

Fig. Changes of PM mass concentrations during fountain candles burning, obtained by Grimm environmental aerosol spectrometer EDM365 (A) and particulate matter sensor SPS30 (B).

Comparing the performance of the different measuring devices, it was determined that the Pod2 device is not appropriate for measuring indoor aerosol particles. The obtained mass concentrations of PM_{10} in the model experiment exceed the 24-h permissible limit value in atmospheric air (50 µg/m^3 established in Latvia) more than 6 times. Most aerosol particles released in the room have a size below 0.265 µm, which are the most harmful to human health.

References

[1] Klepeis, N.E.; Nelson, W.C.; Ott, W.R.; Robinson, J.P.; Tsang, A.M.; Switzer, P.; Behar, J.V.; Hern, S.C.; Engelmann, W.H. *J Expo. Sci. Environ. Epidemiol.* **2001**, *11*, 231–252.

[2] Burden of Disease from Household Air Pollution for 2016. World Health Organization. **2018**.

Section of
Physical Chemistry

USE OF RAMAN SPECTROSCOPY TO DETERMINE THE QUALITY OF GRAPHENE TRANSFERRED ONTO SULPHONATED POLY(ETHER ETHER KETONE) MEMBRANES

Reinis Kaparkalējs[1], Elīna Pajuste[2], Jevgēņijs Gabrusenoks[1],
Einārs Sprūģis[1], Guntars Vaivars[1, 3]

[1] *Institute of Solid State Physics, University of Latvia, Ķengaraga str. 8, Riga, Latvia*
[2] *Institute of Chemical Physics, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[3] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
E-mail: reinis.kaparkalejs@cfi.lu.lv

Separation of hydrogen isotopes is of major importance in both the current and future energy industry. It is well known that graphene is permeable to hydrogen-1, but much less so to deuterium and tritium [1]. This property can be used in construction of electrochemical devices for efficient separation of hydrogen isotopes.

Transfer of graphene from copper foil onto the substrate membrane was accomplished via the hot press method. Several different press temperatures were used. Nafion as well as SPEEK were used as substrate membranes.

The quality of transferred graphene was determined by Raman spectroscopy. Measurements of graphene after transfer were performed on copper foil as well as polymer membrane substrate. Quality of graphene deposits was evaluated by comparing the ratio of the two most characteristic peaks in graphene Raman spectra between samples.

Reference

[1] Bukola, S.; Liang, Y.; Korzeniewski, C.; Harris, J.; Creager, S. *J. Am. Chem. Soc.* **2018**, *140*(5), 1743–1752.

Acknowledgement. Authors acknowledge financial support from ERDF Project No. 1.1.1.1/19/137 “Graphene-based electrochemical pumping system for radioactive hydrogen isotope separation”.

SOLID SOLUTIONS OF MONO AND DIHALOGEN ALKYL PHOSPHONIUM SALT DERIVATIVES AND THEIR PHOTOLUMINESCENCE PROPERTIES

Kristaps Saršūns[1], Igors Kļimenkovs[1], Meldra Ķemere[2], Anatolijs Šarakovskis[2], Agris Bērziņš[1], Toms Rēķis[1]

[1] Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia
[2] Institute of Solid State Physics, University of Latvia, Ķengaraga str. 8, Riga, Latvia
E-mail: kristaps.sarsuns@lu.lv

A neglected crystal engineering strategy that would allow to tune a variety of properties of a crystalline material in continuum is to obtain solid solutions. However, for organic systems, it has been observed that occasionally even very similar molecular entities cannot be interchanged in the crystal lattice. Up to date, there are only some rough, empirical guidelines indicating what kind of binary systems would possibly show component miscibility in the solid state. One type of binary systems deemed to form solid solutions is a system constituting two molecules differing by halogen atom type [1].

In this research work, halogenated alkyl phosphonium salts have been selected to attempt solid solution engineering. The compounds are known to exhibit long-persistent room-temperature solid-state luminescence phenomena [2].

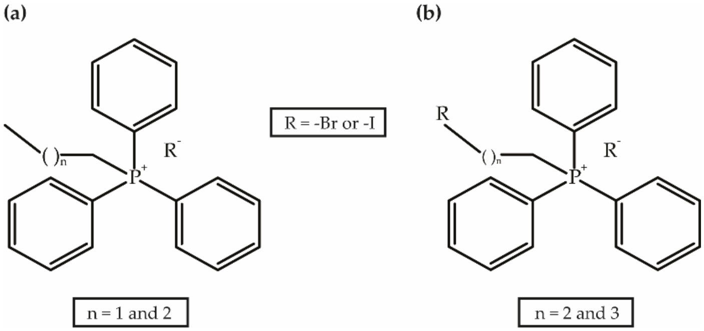


Fig. Molecular structures of mono (a) and dihalogen (b) alkyl phosphonium salt derivatives.

We explored the solid solution formation in binary systems of mono and dihalogen alkyl phosphonium salt derivatives (Fig.). Solid solutions have been identified and characterized using powder X-ray diffraction and thermal methods of analysis. Photoluminescence spectra of the new crystalline phases were studied to explore the differences with respect to the luminescence properties of pure substances known from the literature [2].

References

[1] Corpinot, M.K.; Bučar, D.K. *Cryst. Growth Des.* **2019**, *19*(2), 1426–1453.

[2] Alam, P.; Leung, N.L.C.; Liu, J.; Cheung, T.S.; Zhang, X.; He, Z.; Kwok, R.T.K.; Lam, J.W.Y.; Sung, H.H.Y.; Williams, I.D.; Chan, C.C.S.; Wong, K.S.; Peng, Q.; Tang, B.Z. *Adv. Mater.* **2020**, *32*(22), 2001026.

Acknowledgements. European Social Fund project "Strengthening of the capacity of doctoral studies at the University of Latvia within the framework of the new doctoral model", identification No. 8.2.2.0/20/I/006 and University of Latvia foundation through "Mikrotīkls" doctoral scholarship in the field of natural and medical sciences.

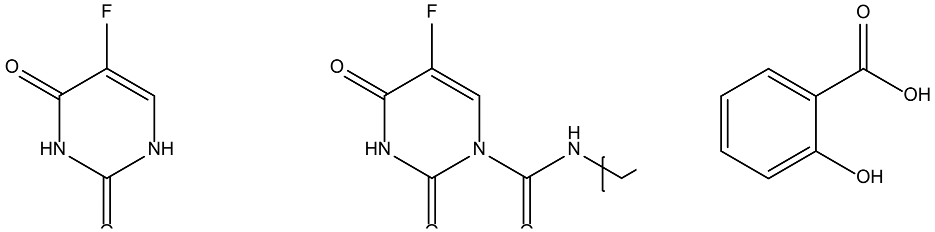
EVALUATION OF PHARMACEUTICAL ACTIVE INGREDIENT ENCAPSULATION PROCESS IN CYCLODEXTRIN BASED METAL ORGANIC FRAMEWORKS

Kristīne Krūkle-Bērziņa, Anatolijs Mishnev

Latvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga, Latvia
E-mail: kkberzina@osi.lv

Metal–organic frameworks (MOFs) have been known for decades, and they continuously have gained increased interest because of their application potential in various fields, such as pharmacy, medicine, technology etc [1]. Porous architecture and adjustable properties of cyclodextrin (CD) MOFs allow them to be considered as promising drug carriers. Modification of the properties of an existing active pharmaceutical ingredient (API) without changing its biological role can be much faster and more effective [2]. Several papers have already reported successful encapsulation of APIs in CD MOFs by adjusting the bioavailability properties of the drug [3].

In this study we explored encapsulation process of APIs in several newly obtained MOFs with structures and properties not yet reported in the literature. For the encapsulation process we selected three different APIs (see Fig.). Several different experimental encapsulation approaches were tested to achieve a successful result. To evaluate the API encapsulation process in the CD MOFs different methods were applied.



A B C

Fig. Molecular structures of the APIs selected for the encapsulation study: A – 5-fluorouracil; B – carmofur; C – salicylic acid.

References

[1] Rajkumar, T.; Kukkar, D.; Kim, K.H.; Sohn, J.R.; Deep, A. *J. Ind. Eng. Chem*. **2019**, *72*, 50–66.

[2] Domingos, S.; André, V.; Quaresma, S.; Martins, I.C.B.; Minas da Piedade, M.F.; Duarte, M.T. *J. Pharm. Pharmacol.* **2015**, *67*, 830–846.

[3] Hartlieb, K.J.; Ferris, D.P.; Holcroft, J.M.; Kandela, I.; Stern, C.L.; Nassar, M.S.; Botros, Y.Y.; Stoddart, J.F. *Mol. Pharmaceutics*. **2017**, *14*, 1831–1839.

Acknowledgement. Project is co-financed by European Regional Development Fund within the Activity 1.1.1.2 “Post-doctoral Research Aid”, research application No. 1.1.1.2/VIAA/3/19/583, “Application of metal-organic frameworks as potential carriers of active pharmaceutical ingredients”.

SURFACE ELECTROCHEMICAL AND PHYSICAL PROPERTIES OF ION-CONDUCTING MEMBRANES

Dmitrijs Bogdanovs[1], **Einārs Sprūģis**[1], **Guntars Vaivars**[1, 2]

[1] Institute of Solid State Physics, University of Latvia, Ķengaraga str. 8, Riga, Latvia
[2] Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia
E-mail: bogdanovsdmitrij@gmail.com

Electrochemical devices (lithium and sodium ion batteries as a priority) use ion-conducting polymer membranes. When forming multilayer structures together with electrodes, their surface properties, which are studied much less, are essential. The work aims to determine the electrochemical properties of the membrane surface (zeta potential) and how they affect the formation of composites by adding new components onto it (ionic liquids, lithium and sodium salts) [1].

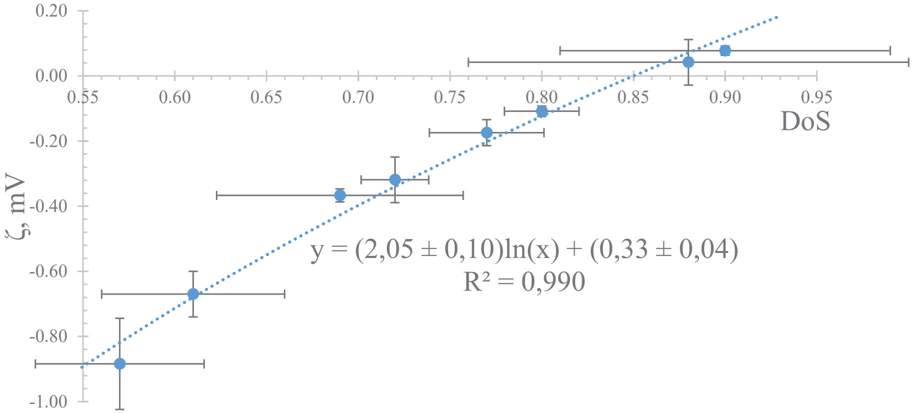


Fig. Measured surface zeta potential as a function of membranes degree of sulfonation, pH = 6.

The preliminary results show that the higher degree of sulfonation is the closer to neutral the surface of the membrane becomes up until the point around 0,85, where negatively charged surface changes to become a positively charged one.

Reference

[1] Vaivars, G.; Bogdanovs, D.; Sprugis, E. *18th Int. Conf. Electroanalysis ESEAC.* **2022**, June 5–9. Vilnius, Lithuania. O-39, p. 86.

Acknowledgement. Authors acknowledge financial support from Latvian Science Council Project No. LZP-2020/1-0391.

SCREENING OF CRYSTALLIZATION ADDITIVES FOR POLYMORPH CONTROL OF P-AMINOBENZOIC ACID

Artjoms Jermakovs, Aina Semjonova
Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia
E-mail: art.jer12@gmail.com

Polymorphism of active pharmaceutical ingredients have been the subject of intense investigation in the drug industry due to their influence on the properties of the drug. A better understanding of the formation of different polymorph forms and control mechanism may improve crystallization process efficiency and reduce production cost [1–2].

In this study, para-aminobenzoic acid (pABA) was used as a model substance to investigate the additive crystallization control approach. pABA has four polymorph forms, which have different types of H-bonding and aromatic interactions (Fig.) [3–4].

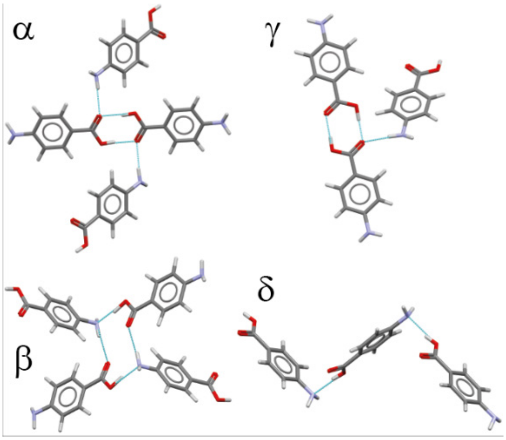


Fig. The four pABA polymorphs with H-bonding interactions.

The crystallization of pABA was explored under different conditions by performing evaporation and cooling crystallization from different solvents. Solid forms obtained in the crystallization were characterized by powder X-ray diffraction. Surfactants, polymers, and different molecular compounds were tested as additives. After evaluation of the results of the crystallization from pure solvents, water was selected for additives screening. Surfactants, polymers, and different molecular compounds were tested as additives.

In most of the cases, the results of crystallization with additive presence were the same as those from the pure solvent. However, polyacrylic acid has shown the potential to form a metastable form by cooling crystallization. Moreover, a new cocrystal was obtained in the presence of nicotinic acid by fast evaporation.

References

[1] Pudipeddi, M.; Serajuddin, A.T.M. Tren *J. Pharm. Sci.* **2005**, *94*(5), 929–939.

[2] Simone, E.; Steele, G.; Nagy, Z.K. *Cryst. Eng. Comm.* **2015**, *17*(48), 9370–9379.

[3] Cruz-Cabeza, A.J.; Davey, R.J.; Oswald, I.D.H.; Ward, M.R.; Sugden, I.J. *Cryst. Eng. Comm.* **2019**, *21*(13), 2034–2042.

[4] Bobrovs, R.; Drunka, L.; Auzins, A.A.; Jaudzems, K.; Salvalaglio, M. *Cryst. Growth Des.* **2021**, *21*(1), 436–448.

Section of Organic Chemistry

DEVELOPMENT OF BENZOXAPHOSPHEPINE 2-OXIDES AS CARBONIC ANHYDRASE INHIBITORS

Anastasija Balašova, Raivis Žalubovskis

Latvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga, Latvia
Faculty of Materials Science and Applied Chemistry,
Institute of Technology of Organic Chemistry, Riga Technical University,
Paula Valdena str. 3/7, Riga, Latvia
E-mail: balasova@osi.lv

Carbonic anhydrases (CA, EC 4.2.1.1) are essential metalloenzymes found across all kingdoms of life. These enzymes are involved in many important physiological processes, as they catalyse the reversible hydration of carbon dioxide [1]. To date, 15 different human CA isoforms have been identified, out of which CA IX and XII isoforms are highly overexpressed in different tumour types and may contribute to the progression of cancer [2]. Therefore, there is a particular need to develop potent and selective CA inhibitors.

Herein we report our results on the development of a new class of CA inhibitors – benzoxaphosphepine 2-oxides. Aforementioned compounds showed a remarkable selectivity and good activity against the tumour-associated isoforms CA IX and XII [3]. Furthermore, these compounds can be used as starting points for the design of more potent CA IX/XII inhibitors.

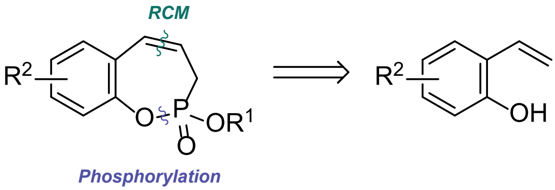


Fig. Retrosynthesis of target compounds.

References

[1] Supuran, C.T. *Metabolites*. **2018**, *8*, 25.
[2] Singh, S.; Lomelino, C.L.; Mboge, M.Y.; Frost, S.C.; McKenna, R. *Molecules*. **2018**, *23*, 1045.
[3] Pustenko, A.; Balašova, A.; Nocentini, A.; Supuran, C.T.; Žalubovskis, R. *J. Med. Chem.* **2023**, *38*, 216–224.

Acknowledgements. This project has been supported by the European Social Fund within the Project No. 8.2.2.0/20/I/008 and by the Latvian Institute of Organic Synthesis under internal student grant IG-2023-09.

ACRAB-TOLC EFFLUX PUMP INHIBITOR ANALOG SYNTHESIS

Laura Pauniņa[1], Cristina Durante Cruz[2], Marina Madre[1], Tania Szal[3], Päivi Tammela[2], Aigars Jirgensons[1], Björn Windshügel[3], Jānis Veliks[1]

[1] *Latvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga, Latvia*
[2] *Drug Research Program, Division of Pharmaceutical Biosciences, Faculty of Pharmacy, University of Helsinki, Finland P. O. Box 56 (Viikinkaari 5E), FI-00014, Helsinki, Finland*
[3] *Discovery Research Screening Port, Fraunhofer Institute for Translational Medicine and Pharmacology ITMP, Schnackenburgallee 114, 22525 Hamburg, Germany*
E-mail: laura.paunina@osi.lv

Bacterial resistance to the existing classes of antibiotics is one of the most important challenges for the future healthcare system and bacterial cells efflux pumps play an important role for this internal drug resistance. To reduce the ability of the efflux pumps binding to medication substrates, the molecules called efflux pump inhibitors are used to rejuvenate the antibiotics activity by binding to the efflux pump protein [1].

In the framework of the project, it was hypothesized that AcrAB-TolC efflux pump outer membrane protein TolC in Gram-negative E. coli bacteria cells could represent an attractive drug target. Therefore, structure analogs of known clinical candidate compound have been synthesized and identified their structure-activity relationships (SAR) to TolC efflux pump [2].

References

[1] AlMatar, M.; Albarri, O.; Makky, E.A.; Köksa, F. *Pharmacol. Rep.* **2021**, *73*, 1–16.

[2] Ott, G.R.; Cheng, M.; Learn, K.S.; Wagner, J.; Gingrich, D.E.; Lisko, J.G.; Dorsey, B.D. *J. Med. Chem.* **2016**, *59*(16), 7478–7496.

Acknowledgements. This project was supported under the framework of the JPIAMR – Joint Programming Initiative on Antimicrobial Resistance. B. W. was supported the German Federal Ministry for Education and Research (01KI1827A). A. J. was supported by the state education development agency (1.1.1.5/ERANET/19/03), C. D. C. and P. T. were supported by the Academy of Finland (Grant No. 326261).

SYNTHESIS OF POTENTIAL IRE1α INHIBITORS

Jānis Šadauskis[1, 2], Igors Kļimenkovs[2], Edgars Sūna[1]

[1] Latvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga, Latvia
[2] Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia
E-mail: janis.sadauskis@lu.lv

Cancer has a major impact on society around the world and it is one of the leading causes of death. IRE1α is an enzyme that plays a part in the development of certain cancers, such as breast cancer, colon cancer, and prostate cancer. IRE1α inhibitors might be used to treat these types of cancer [1].

The aim of this study was to find IRE1α inhibitors that would have a greater selectivity and bioavailability than the previously discovered ones. Based on computational data about the activity of compound 4f, it was chosen as the model compound for further synthesis.

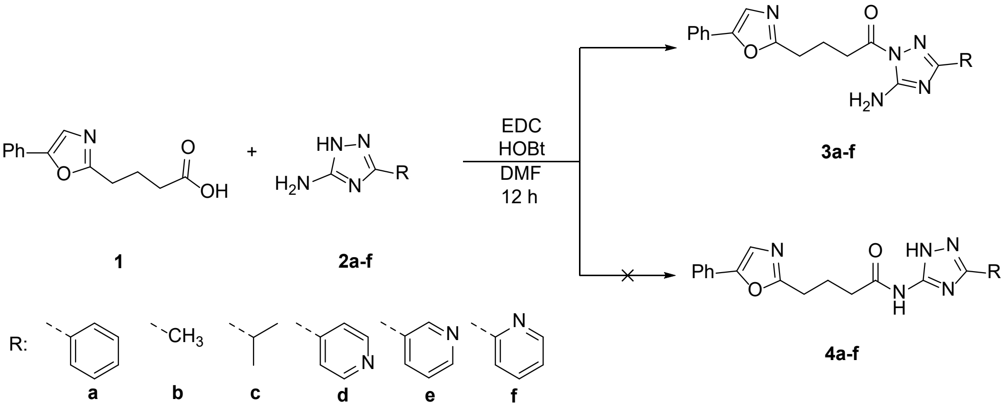


Fig. Synthesis of target compounds **4a-f**.

The reaction used for the synthesis of compound 4f and its analogues was found to yield endocyclically acylated 1,2,4-triazol-5-amines instead of the anticipated exocyclically acylated compounds, but isomerization of endocyclically acylated 1,2,4-triazol-5-amines yielded exocyclically acylated compounds. However, limited hydrolytic stability of compounds 3a-f suggested that the inhibitory activity of these compounds could be mainly due to the presence of compounds 2a-f in solution. Indeed, compound 2f had the greatest ability to inhibit IRE1α out of all the synthesized compounds.

Reference

[1] Madden, E.; Logue, S.E.; Healy, S.J.; Manie, S.; Samali, A. *Biol. Cell.* **2019**, *111*(1), 1–17.

SYNTHESIS OF QUINAZOLINES AND INDAZOLES FROM

Vitalii Solomin[1, 2], **Darija Zaharova**[2, 3]

[1] *Riga Technical University, Paula Valdena str. 3, Riga, Latvia*
[2] *Latvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga, Latvia*
[3] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
E-mail: vitalijs.solomins@osi.lv

New mild methods for the synthesis of indazole and quinazoline has been studied and developed. Using novel protocols, 2-formylphenylboronic acids **1** can be converted to the heterocycles of interest in a good yield.

For quinazoline **3** synthesis, guanidines and amidines **2** can be used [1]. Reaction proceeds in alcoholic media with Cu(I) iodide as a catalyst (Chan-Evans-Lam reaction conditions [2]).

With dialkyl azodicarboxylates **4** and dialkyl hydrazinedicarboxylates **5** *N*-protected indazoles **6** can be synthesized [3]. Two-step protocol involves coupling, mediated by Cu(II) acetate, with subsequent one-pot conversion of formed semi-product to indazole in acidic media.

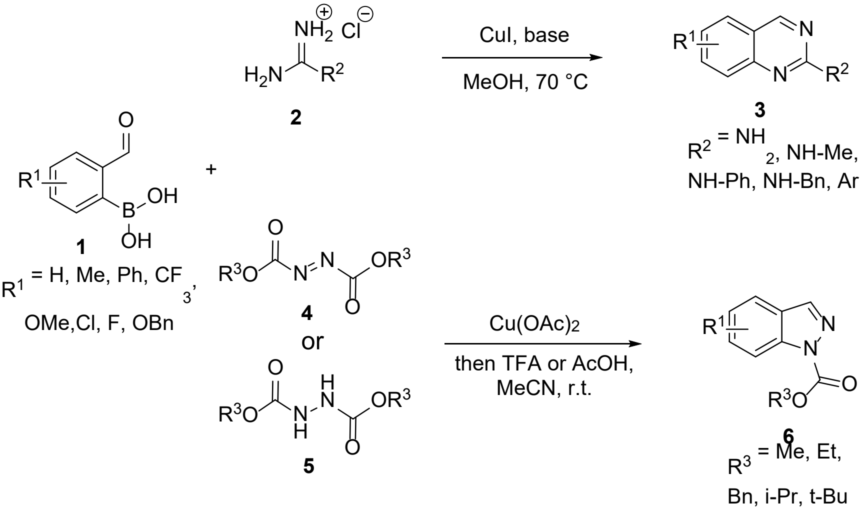


Fig. Synthesis of quinazolines and *N*-protected indazoles.

Present approach suggests 2-formylphenylboronic acids as a multi-purpose building blocks for a convenient access towards fused nitrogen-containing heterocycles.

References

[1] Solomin, V.V.; Seins, A.; Jirgensons, A. *Synlett.* **2020**, *31*, 1507.
[2] Chan, D.M.T.; Monaco, K.L.; Wang, R.-P.; Winters, M.P. *Tetrahedron Letters.* **1998**, *39*, 2933.
[3] Solomin, V.V.; Seins, A.; Jirgensons, A. *RSC Advances.* **2021**, *11*, 22710.

AZIDE-TETRAZOLE EQUILIBRIUM IN PYRIDO[3,2-*d*] PYRIMIDINES

Kristaps Leškovskis, Irina Novosjolova, Māris Turks
Institute of Technology of Organic Chemistry, Faculty of Materials Science and Applied Chemistry, Riga Technical University, P. Valdena str. 3, Riga, Latvia
E-mail: kristaps.leskovskis@rtu.lv

Heterocycles with an azido-azomethine structural entity are interesting due to their intrinsic dynamic azide-tetrazole tautomeric equilibrium in the solution phase [1] alongside rich azide functional group chemistry [2].

Herein, a method for the synthesis of 5-substituted tetrazolo[1,5-*a*]pyrido[2,3*e*] pyrimidines from 2,4-diazidopyrido[3,2-*d*]pyrimidine in S_NAr reactions with *N*-, *O*-, and *S* nucleophiles is presented [3]. The tetrazolo[1,5-*a*]pyrimidine derivatives can be regarded as 2azidopyrimidines due to present azide-tetrazole valance tautomerism and functionalized in copper(I)-catalyzed azide-alkyne dipolar cycloaddition (CuAAC) and Staudinger reactions.

Equilibrium constants and thermodynamic values were determined using variable temperature ^{1}H NMR and were found to be $\Delta G_{298} = -3.33$ to -7.52 (kJ/mol), $\Delta H = -19.92$ to -48.02 (kJ/mol) and $\Delta S = -43.74$ to -143.27 (J/mol·K). The negative Gibbs free energy values assert tetrazole as the major tautomeric form in solutions. Furthermore, the key starting material 2,4-diazidopyrido[3,2-*d*]pyrimidine shows a high degree of tautomerization in different solvents presenting up to 7 tautomeric forms.

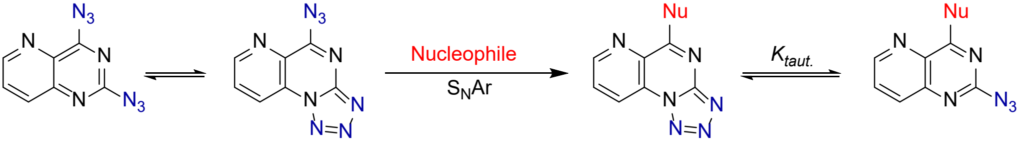


Fig. Azide-tetrazole equilibrium guided S_NAr reaction of azidopyrimidines.

References

[1] a) Sebris, A.; Turks, M. *Chem. Heterocycl. Compd.* **2019**, *55*, 1041–1043. b) Tišler, M. *Synthesis.* **1973**, *1973*, 123–136. c) Leškovskis, K.; Mishnev, A.; Novosjolova, I.; Turks, M. *J. Mol. Struct.* **2022**, *1269*, 133784. d) Cmoch, P.; Korczak, H.; Stefaniak, L.; Webb, G.A. *J. Phys. Org. Chem.* **1999**, *12*, 470–478. e) Thomann, A.; Zapp, J.; Hutter, M.; Empting, M.; Hartmann, R.W. *Org. Biomol. Chem.* **2015**, *13*, 10620–10630.

[2] Bräse, S.; Banert, K. *Organic Azides: Syntheses and Applications*; John Wiley & Sons, Ltd.: Chichester, UK, **2009**, ISBN 9780470682517.

[3] Leškovskis, K.; Mishnev, A.; Novosjolova, I.; Turks, M. *Molecules.* **2022**, *27*, 7675.

Acknowledgements. The authors thank the Latvian Council of Science Grant LZP2020/10348 for financial support. K. L. thanks the European Social fund within project No. 8.2.2.0/20/I/008.

SYNTHETHIC PATHWAYS TOWARDS PURINE DERIVATIVE AS A POTENTIAL MOLECULAR SYSTEM FOR THE PHOTO-CATALYSIS

Aleksejs Burcevs, Irina Novosjolova

Faculty of Materials Science and Applied Chemistry, Riga Technical University,
P. Valdena str. 3, Riga, Latvia
E-mail: aleksejs.burcevs@rtu.lv

Fluorescent purine derivatives have a variety of uses in analytics, such as metal ion [1] and pH sensors [2], as well they are used for cell imaging [3] and as photo-catalysts [4].

Target purine compound **2** was designed with an aim to be used as a potential system for photo-catalysis. For the synthesis of **2**, derivatization of *C*(6), *C*(8) and *N*(9) positions of 6-chloropurine (**1**) with **A**, **B** and **C** moieties is required. Several synthetic pathways were designed and have been tested. In the end, target compound **2** was obtained, using the combinations of S_NAr, S_N2, CuAAC, C-C metal catalyzed coupling, alkylation and Mitsunobu reactions and these results will be discussed.

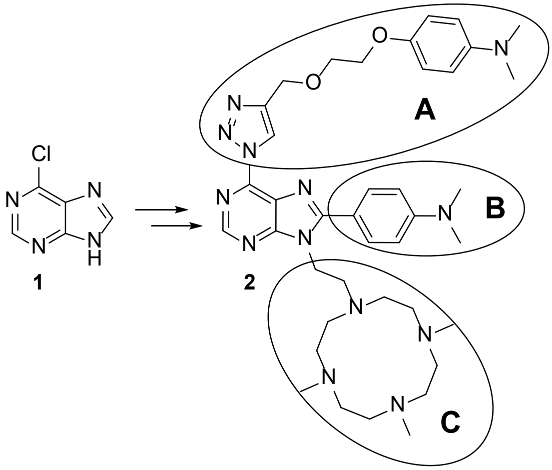


Fig. Starting material **1** and target compound **2**.

References

[1] Jovaisaite, J.; Cīrule, D.; Jeminejs, A.; Novosjolova, I.; Turks, M.; Baronas, P.; Komskis, R.; Tumkevicius, S.; Jonusauskas, G.; Jursenas, S. *Phys. Chem. Chem. Phys.* **2020**, *22*, 26502–26508.

[2] Sun, K.M.; McLaughlin, C.K.; Lantero, D.R.; Manderville, R.A. *J. Am. Chem. Soc.* **2007**, *129*, 1894–1895.

[3] Šišuļins, A.; Bucevičius, J.; Tseng, Y.; Novosjolova, I.; Traskovskis, K.; Bizdēna, Ē.; Chang, H.; Tumkevičius, S.; Turks, M. *Beilstein J. Org. Chem.* **2019**, *15*, 474–489.

[4] Kumar, A.; Mital, S. *J. Mol. Catal. A Chem.* **2004**, *219*, 65–71.

Acknowledgement. The authors thank MEPS co-project LV-LT-TW/2022/9 for financial support.

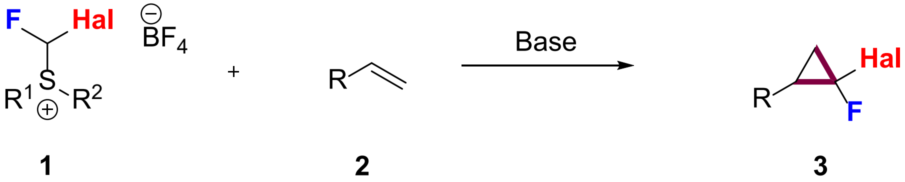
FLUOROHALOMETHYLSULFONIUM SALTS AS A NOVEL FLUOROHALOCARBENE SOURCE

Artūrs Sperga, Jānis Veliks

Latvian Institute of Organic Synthesis, Aizkraukles str., 21, Riga, Latvia
Faculty of Materials Science and Applied Chemistry Riga Technical University,
Paula Valdena str. 3/7, Riga, Latvia
E-mail: arturs.sperga@inbox.lv

Synthesis of fluorine containing molecules is of great interest due to its unique properties and vast application in pharmaceuticals, agrochemicals and materials [1].

Previously in our group we have developed fluoromethylene transfer from fluromethylsulfonium salts [2, 3]. Herein we wish to report preliminary results on synthesis of reagents **1** and its initial application in carbene transfer reaction (Fig.).



Hal = Cl, Br, I

Fig. Alkene cyclopropanation with fluorohalomethylsulfonium salts.

We have found that functionalized sulfonium salts – fluorohalomethylsulfonium reagents **1** are efficient source of fluorhalocarbene under basic conditions and they undergo unactivated alkene **2** cyclopropanation to deliver fluorohalocyclopropanes **3**.

References

[1] Zhou, Y.; Wang, J.; Gu, Z.; Wang, S.; Zhu, W.; Aceña, J.L.; Soloshonok, V.A.; Izawa, K.; Liu, H. *Chem. Rev.* **2016**, *116*, 422–518.

[2] Melngaile, R.; Veliks, J. *Synthesis.* **2021**, *53*, 4549–4558.

[3] Sperga, A.; Zacs, D.; Veliks, J. *Org. Lett.* **2022**, *24*, 4474–4478.

DESIGN OF S AND SE CONTAINING NUCLEOPHILIC CATALYSTS

Oto Filipsons[1, 2], **Artis Kinēns**[1, 2]
[1] *Latvian Institute of Organic Chemistry, Aizkraukles str. 21, Riga, Latvia*
[2] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
E-mail: otofilipsons@osi.lv

Pyridine and its derivatives are often used as effective nucleophilic catalysts for reactions such as *the Baylis-Hillman* reaction, acyl group transfer reactions and others. A noteworthy example is DMAP which is a widely known acylation reaction catalyst. Alcohol acylation reactions can also be catalysed by isochalcogenurea derivatives which exhibit a 1,5-O···Ch interaction in the acylated intermediates [1]. Similar chalcogen bonding interactions haven't been investigated in DMAP-type catalysts.

In this research chalcogen containing DMAP-type catalysts were synthesized. Activities of the newly obtained catalysts were determined by performing an acylation reaction of a sterically hindered secondary alcohol (Fig.). Experiments show that introducing a substituent at the C-2 position significantly decreases the catalytic activity which was expected and has been previously reported [2]. Importantly, it was observed that the activity of sulfur-containing catalysts increases with increasing electron donating ability of the C-4 substituent of pyridine, but the opposite trend was observed for selenium-containing catalysts.

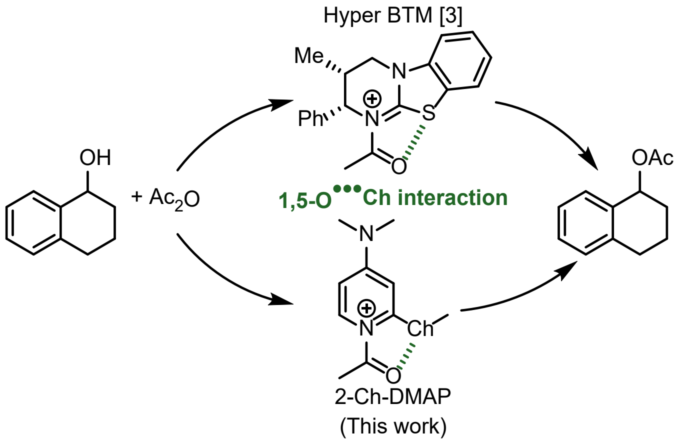


Fig. Acylation of a sterically hindered 2° alcohol using Lewis base catalysis.

References

[1] Young, C.M.; Elmi, A.; Pascoe, D.J.; Morris, R.K.; McLaughlin, C.; Woods, A.M.; Frost, A.B.; Houpliere, A.; Ling, K.B.; Smith, T.K.; Slawin, A.M.Z.; Willoughby, P.H.; Cockroft, S.L.; Smith, A.D. *Angew. Chem. Int. Ed.* **2020**, *59*(9), 3705–3710.
[2] Vedejs, E.; Chen, X. *J. Am. Chem. Soc.* **1997**, *119*(10), 2584–2585.
[3] Merad, J.; Pons, J.-M.; Chuzel, O.; Bressy, C. *Eur. J. Org. Chem.* **2016**, *2016*(34), 5589–5610.

SYNTHESIS OF LOW-ABUNDANCE SESQUITERPENOIDS FROM BCARYOPHYLLENE

Georgijs Stakanovs, Dace Rasiņa, Aigars Jirgensons
Latvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga, Latvia
E-mail: georgijs.stakanovs@osi.lv

β-Caryophyllene is one of the most abundant sesquiterpenes found in nature, therefore it is available at low price from several commercial sources. The unusual structure of βcaryophyllene with two stereodefined chiral centers renders this terpene an attractive renewable starting material for the access of diverse high value compounds.

We demonstrate that β-caryophyllene and its oxide can be used in synthesis of biologically active sesquiterpene lactones rumphellaones A-C [1], disesquiterpenoid rumphellolide J [2], and linariophyllene B (scheme 1). In our ongoing research we show that rare structural units, such as propellane **1**, bridgehead olefins **2a, b** and epoxides **3a, b** (Fig.) can be prepared from βcaryophyllene in a stereoselective fashion [3]. Such compounds can serve as reference standards for the analysis of constituents of various plant extracts.

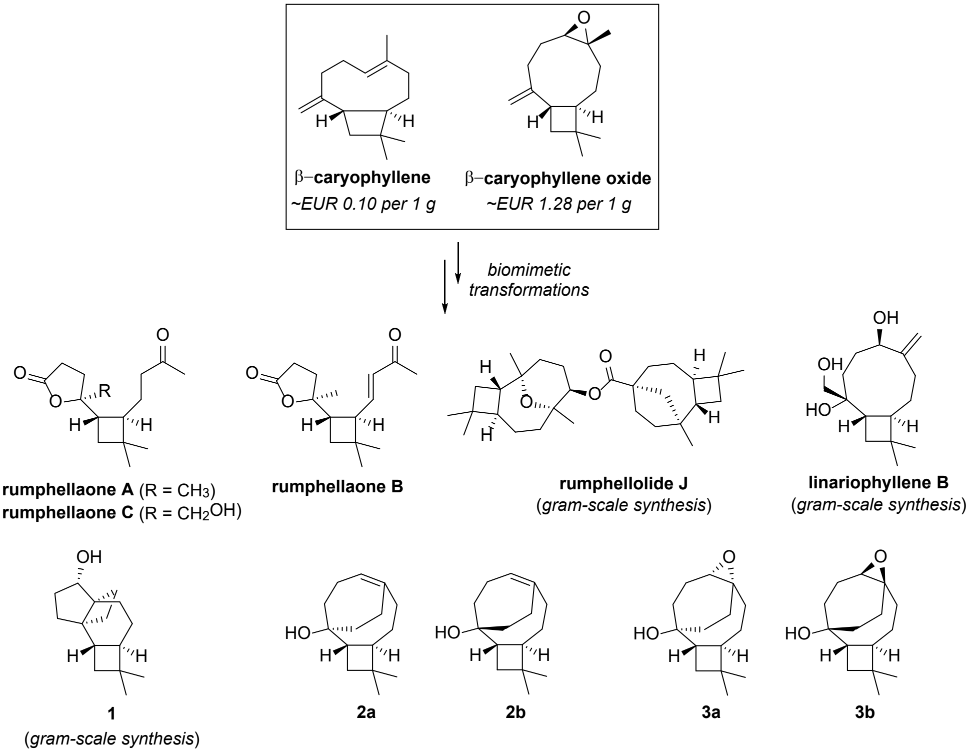


Fig. Diverse semisynthesis of natural products from β-caryophyllene and its oxide.

The biomimetic transformations employed in several chemical steps elucidate the possible biosynthetic route towards natural sesquiterpenoids. Structures of final products were unambiguously confirmed by single crystal X-ray diffraction analysis.

References

[1] Stakanovs, G.; Mishnev, A.; Rasina, D.; Jirgensons, A. *J. Nat. Prod.* **2020**, *83*, 2003.

[2] Stakanovs, G.; Belyakov, S.; Jirgensons, A.; Rasina, D. *Org. Biomol. Chem.* **2022**, *20*, 2455.

[3] Manuscript in preparation.

THE SYNTHESIS OF OCTAHYDROINDOLOQUINOLIZINES VIA IODINE-PROMOTED OXIDATION/ BISHLER-NAPIERALSKI CYCLISATION SEQUENCE

Niklāvs Ūdris, Gints Šmits

Latvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga, Latvia
E-mail: niklavs@osi.lv

Octahydroindoloquinolizine is a common structural motif in corynanthe-type indole alkaloids. These natural products possess a broad scope of pharmacological activities. Members of this natural product family are known to be α_1-adrenergic and opioid receptor antagonists as well as exhibit cytotoxicity in various cancer cell lines.

Octahydroindoloquinolizines are typically prepared *via* Bishler-Napieralski or Pictet-Spengler cyclization reactions. In course of our studies, we found that these transformations are often low yielding and sluggish on structurally complex substrates and alternative mild protocols are highly desirable. After an extensive screening of reaction conditions, we found that elemental iodine [1] is a good oxidant for the preparation of lactams **3** in good yields starting from the corresponding tertiary amines **1c**. These intermediates **3** were further subjected to mild Bishler-Napieralski cyclization conditions furnishing the target octahydroindoloquinolizines. Interestingly, in the unprotected **1a** or TBS-protected substrates **1b** indole ring tends to oxidize first leading to spirocycles **2**.

The mechanistic aspects of the developed reaction sequence as well as its application in the total syntheses of corynanthe-type indole alkaloids will be presented.

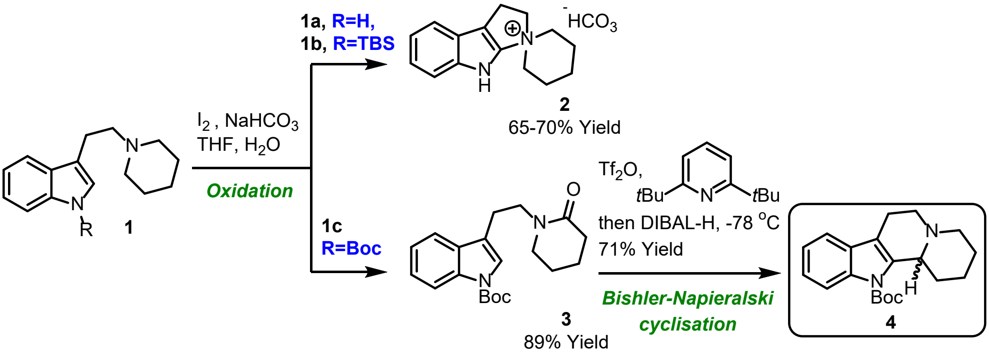


Fig. Octahydroindoloquinolizine preparation *via* iodine-promoted oxidation/ Bishler-Napieralski sequence.

Reference

[1] Griffiths, R.J.; Burley, G.A.; Talbot, E.P.A. *Org. Lett.* **2017**, *19*, 870–873.

Acknowledgement. The authors acknowledge the individual fellowship project of the Latvian Council of Science No. lzp-2020/2-0045 for the financial support.

C-H ARYLATION OF PENTACYCLIC TRITERPENOIDS

Vladislavs Krošķins, Jevgeņija Lugiņina, Māris Turks

Faculty of Materials Science and Applied Chemistry, Institute of Technology of Organic Chemistry, Riga Technical University, P. Valdena str. 3, Riga, Latvia
E-mail: vladislavs.kroskins@rtu.lv

Naturally abundant pentacyclic triterpenoids are significant 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, ursolic acids and betulin, are the most recognizable compounds of this branch, which are isolated from various plants. The aim of this work is to obtain novel triterpenoic derivatives by C-H arylation at C(22). For this purpose, precursors bearing picolinic amide directing groups were synthesized.

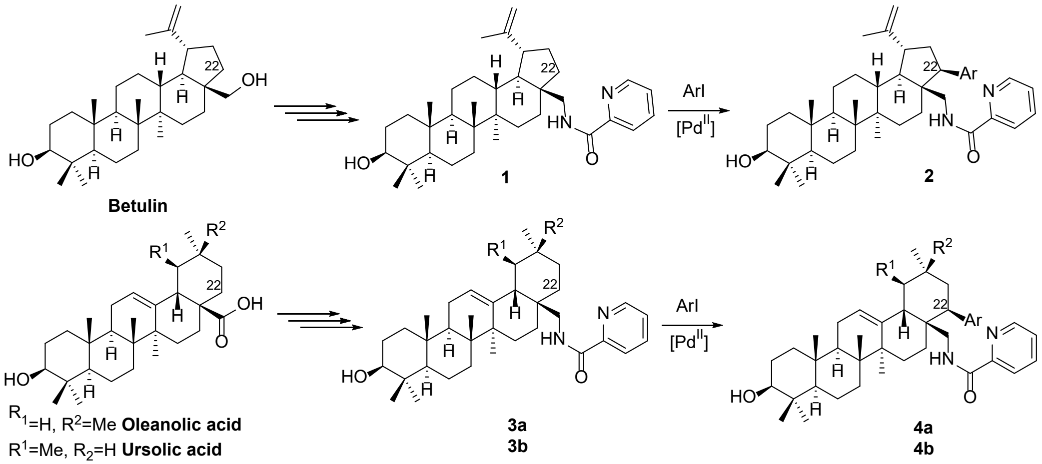


Fig. C-H activation of betulin, oleanolic acid and ursolic acid.

Obtained picolinic amides **1**, **3a**, **3b** were successfully combained with aryl iodides employing Daugulis conditions and C-H arylated products **2**, **4a**, **4b** were obtained [5].

References

[1] Sheng, H.; Sun, H. *Nat. Prod. Rep.* **2011**, *28*, 543–593.

[2] Teodoro, T.; Zhang, L.; Alexander, T.; Yue, J.; Vranic, M.; Volchuk, A. *FEBS Lett.* **2008**, *582*, 1375–1380.

[3] Huguet, A.I.; del Carmen Recio, M.; Máñez, S.; Giner, R.M.; Ríos, J.L. *Eur. J. Pharmacol.* **2000**, *410*, 69–81.

[4] Dang, Z.; Lai, W.; Qian, K.; Ho, P.; Lee, K.H.; Chen, C.H.; Huang, L. *J. Med. Chem.* **2009**, *52*, 7887–7891.

[5] Zaitsev, V.G.; Shabashov, D.; Daugulis, O. *J. Am. Chem. Soc.* **2005**, *127*, 13154–13155.

COBALT-CATALYZED C(SP^2)-H BOND ALLYLATION

Emīls Edgars Bašēns, Aleksandrs Čižikovs, Liene Grigorjeva

Latvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga, Latvia
E-mail: emils.edgars.basens@osi.lv

In the last couple of decades, high-valent cobalt catalysis has been used as a valuable tool for C-H bond activation and functionalization [1]. The use of cobalt(II) salt catalysts in combination with bidentate directing groups has proven to be an effective strategy for various C-H bond transformations [2, 3]. With cobalt being less expensive alternative to noble metals, it also displays unique reactivity and regioselectivity [4].

Allyl-functional groups are important in organic synthesis as they open the door to many further modifications of the substrate. Employing cobalt catalyzed C-H bond allylation on amino acid derivatives **1**, it is possible to utilize cheap reagents to obtain useful building blocks for other synthetic applications. Using optimization of cobalt catalysts, solvents, oxidants, additives and allylation reagents we were able to obtain diallylated phenylalanine derivative **2** in good yield.

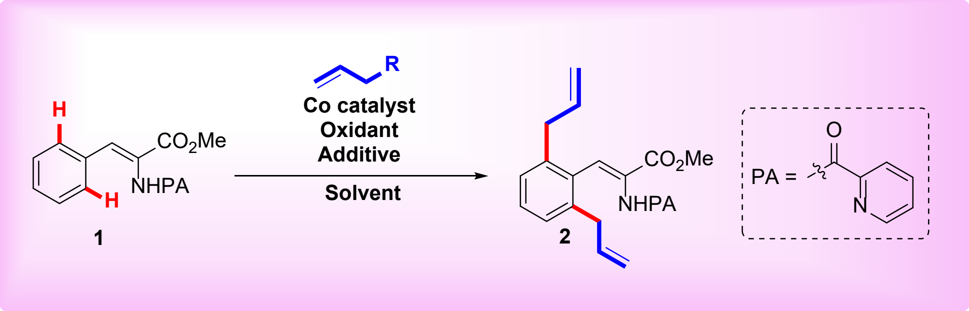


Fig. Current work on allylation of phenylalanine derivatives **1**.

References

[1] Lukasevics, L.; Cizikovs, A.; Grigorjeva, L. *Chem. Commun.* **2021**, *57*, 10827–10841.
[2] Lukasevics, L.; Cizikovs, A.; Grigorjeva, L. *Org. Lett.* **2021**, *23*(7), 2748–2753.
[3] Lukasevics, L.; Cizikovs, A.; Grigorjeva, L. *Chem. Commun.* **2022**, *58*, 9754–9757.
[4] Gandeepan, P.; Muller, T.; Zell, D.; Cera, G.; Warratz, S.; Ackermann, L. *Chem. Rev.* **2019**, *119*(4), 2192.

Acknowledgement. This research is funded by Latvian Institute of Organic synthesis internal grant No. IG-2023-05.

EXPLORING THE REACTIVITY OF C(SP^2)-H ACTIVATED AMINO ACID COBALT COMPLEXES: A FACILE ROUTE TOWARDS INDOLES

Aleksandrs Čižikovs, Liene Grigorjeva

Latvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga, Latvia
E-mail: aleksandrs.cizikovs@osi.lv

In the last few decades transition metal-catalyzed direct C-H bond functionalization has served as a valuable tool for the construction of complex molecules from more simple starting materials, mainly due to its atom- and step-economical nature [1]. Nowadays, the field of third row transition metal catalyzed C-H functionalization is being extensively studied as a cheaper and attractive alternative to noble metal catalysts [2].

Our current work is dedicated to the development of cobalt-catalyzed picolinamide-directed C-H bond functionalization of amino acid derivatives. Starting from α,β-unsaturated amino acids **1** we were able to synthesize different C-H activated Co(III) complexes **2** in very good yields (Fig.). Moreover, using *N*-fluorobenzenesulfonimide, indole **3** derivatives can be obtained.

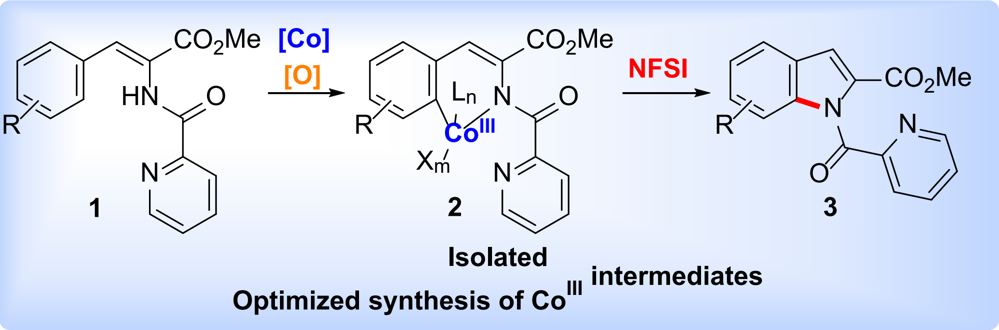


Fig. Cobalt-catalyzed, picolinamide-directed indole **3** synthesis.

References

[1] Gandeepan, P.; Muller, T.; Zell, D.; Cera, G.; Warratz, S.; Ackermann, L. *Chem. Rev*. **2019**, *119*(4), 2192.

[2] Lukasevics, L.; Cizikovs, A.; Grigorjeva, L. *Chem. Commun.* **2022**, *58*, 9754–9757.

Acknowledgement. This research is funded by Latvian Institute of Organic synthesis internal grant No. IG-2023-05.

USE OF TERMINALLY FUNCTIONALIZED PROPARGYL SILANES FOR THE SYNTHESIS OF VARIOUS 5-MEMBERED HETEROCYCLES VIA 1,2-SILYL MIGRATION

Rasma Kroņkalne, Rūdolfs Beļaunieks, Artjoms Ubaidullajevs, Māris Turks
Faculty of Materials Science and Applied Chemistry,
Institute of Technology of Organic Chemistry,
Riga Technical University, P. Valdena str. 3, Riga, Latvia
E-mail: rasma.kronkalne@rtu.lv

Small heterocycles, particularly those containing a 5-membered cycle, are popular motifs in pharmaceuticals, displaying a broad range of biological properties [1]. A well-established strategy for the synthesis of 5-membered saturated/partially saturated heterocycles involves intramolecular cyclization, made possible by internal nucleophile attack on carbocations.

In this work we investigate the use of electrophile induced 1,2-silyl migration in terminally functionalized propargyl silanes to generate stabilized carbocations, capable of reacting with various internal nucleophiles, forming heterocyclic units (Fig.). Various nucleophilic species could be utilized, namely alcohols, carboxylic acids, oximes, acyl and sulfonyl amides, carbamates and thioacetates.

The synthetic utility of the cyclization products was demonstrated by difunctionalization of the alkene moiety in cross-coupling reactions to selectively obtain trisubstituted alkenes. The resulting heterocycle derivatives were obtained with a high degree of stereoselectivity and yields up to 82%.

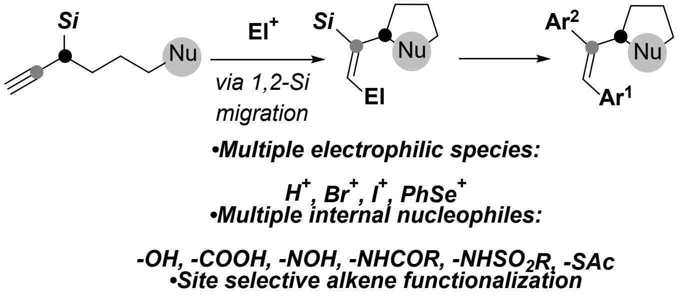


Fig. Heterocyclization of propargyl silanes.

Reference

[1] Vitaku, E.; Smith, D.T.; Njardarson, J.T. *J. Med. Chem.* **2014**, *57*, 10257–10274.

USE OF PROPARGYLSILANES FOR THE PREPARATION OF HIGHLY FUNCTIONALIZED ALKENES VIA 1,2-SILYL MIGRATION

Rūdolfs Beļaunieks, Mikus Puriņš, Rebeka Anna Līpiņa, Māris Turks

Faculty of Materials Science and Applied Chemistry, Riga Technical University,
P. Valdena str. 3, Riga, Latvia
E-mail: rudolfs.belaunieks@rtu.lv

The ease of the unsaturated system reactivity proceeding via β-silyl carbocation ion can be explained by the stabilizing effects of the silicon-carbon bond interaction with carbocation ion – known as β-silicon effect. This can be achieved by either vertical (hyperconjugation) or non-vertical (formation of cyclic silonium ion) stabilization. The formation of the latter, in combination with other stabilizing effects, causes 1,2-silyl migration [1].

Previously, we have reported the use of Brønsted acid to catalyze reactions of propargyl silanes to form various silyl dienes and indenes [2, 3]. Herein, we report the expanded use of the concept by using electrophilic bromine to induce the formation of the reactive allylic cation that readily reacts with a variety of nucleophilic solvents like methanol, dimethylformamide, and acetic acid to form allyl functionalized vinyl silanes.

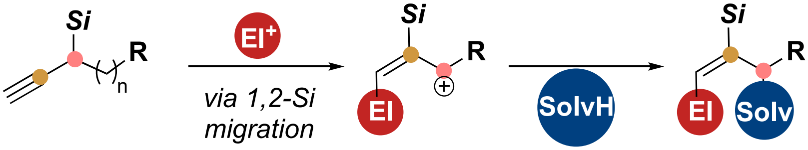


Fig. General scheme of electrophile-induced propargyl silane transformation with solvents.

Use and the functionality of the obtained vinyl silanes are showcased in a variety of transition metal-catalyzed transformations like Suzuki-Miyaura coupling, C-H activation, electrophilic silicon exchange reaction, and Lewis acid-promoted intramolecular cyclization to form indenes.

References

[1] Belaunieks, R.; Puriņš, M.; Turks, M. *Synthesis.* **2020**, *52*, 2147.

[2] Puriņš, M.; Mishnev, A.; Turks, M. *J. Org. Chem.* **2019**, *84*, 3595.

[3] Belaunieks, R.; Puriņš, M.; Kumpiņš, V.; Turks, M. *Chem. Heterocycl. Compd.* **2021**, *57*, 20.

Acknowledgements. This work was supported by European social fund within the project No. 8.2.2.0/20/I/008 and Riga Technical University doctoral student grant.

ELECTROCHEMICAL DECARBOXYLATION OF *N*-SUBSTITUTED 2-AMINOMALONIC ACID MONOESTERS IN INTERMOLECULAR HOFER-MOEST REACTION

Katrīna Prāne, Oļesja Koleda

Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia
Latvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga, Latvia
E-mail: katrina.prane@gmail.com

One of the oldest methods in electroorganic synthesis is Kolbe reaction, where alkyl radical is generated upon anodic decarboxylation [1]. In contrast, Hofer-Moest reaction provides a carbocation after anodic decarboxylation followed by a reaction with a nucleophile [2, 3].

Aminomalonic acid derivatives are readily available substrates that can be relatively easily functionalized, e.g. by alkylation reactions. Herein we report a previously unreported intramolecular Hofer-Moest reaction of *N*-substituted 2-aminomalonic acid monoesters. A stabilized cation **2** is formed after anodic decarboxylation of a malonic acid monoester **1** followed by intramolecular cyclization. The developed method allows to obtain new tetrahydrofurane and tetrahydropyrane fragment containing amino acid derivatives **3** in good yields (Fig.).

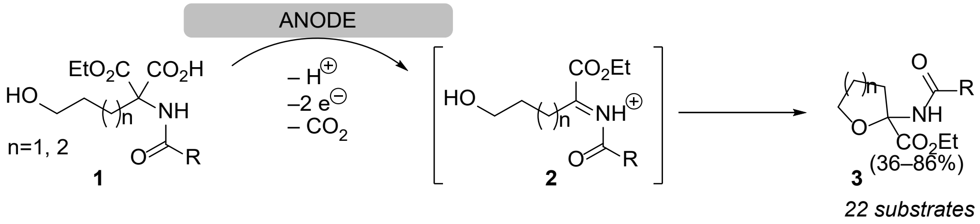


Fig. Intramolecular Hofer-Moest reaction of *N*-substituted 2-aminomalonic acid monoesters.

References

[1] Kolbe, H. *Ann. Chem. Pharm.* **1848**, *64*, 339.
[2] Hofer, H.; Moest, M. *Justus Liebigs Ann. Chem.* **1902**, *323*, 284.
[3] Ramadoss, V.; Zheng, Y.; Shao, X.; Tian, L.; Wang, Y. *Chem.–Eur. J.* **2021**, *27*, 3213.

IMPURITY-INDUCED PHOSPHORESCENCE IN CARBAZOLE DERIVATIVES

Artūrs Mazarevics[1, 2], **Kaspars Leduskrasts**[1], **Edgars Sūna**[1, 2]
[1] *Latvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga, Latvia*
[2] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
E-mail: arturs.mazarevics@osi.lv

Phosphorescence is a type of luminescence in which the emission lifetime is longer than 1 µs. Usually, phosphorescence is exhibited by metal containing compounds, but the high toxicity and manufacturing costs as well as low stability limits the use of such materials. To overcome these drawbacks purely organic phosphorescent materials recently have become popular because of their biocompatibility, low cost, and limitless design possibilities [1].

Carbazole **1** subunit is a widely used moiety in the field of purely organic phosphorescence, but in 2021 it was shown that commercially available carbazole has an isomeric impurity – benzo[*f*]indole **2**, which is responsible for the phosphorescence obtained from carbazole containing luminophores [2]. Herein, we report the synthesis of carbazoles **3b**–**7b** in which the carbazole ring was formed through *Clauson-Kaas* cyclization, thus avoiding commercial impurities. Initially, carbazoles **3b**–**7b** showed phosphorescence, however, after laborious purification, it disappeared. This led us to believe, that a byproduct in the *ClausonKaas* cyclization was responsible for the phosphorescence. Therefore, we created a series of two component systems, where carbazole derivatives **3b**–**7b** were used as hosts and byproducts **3c**–**7c** and **3d**–**7d** as dopants. The two component systems where the indole derivatives **3c**–**7c** were used as dopants, didn't exhibit phosphorescence. Meanwhile employing benzo[*b*]carbazole derivatives **3d**–**7d** as dopants resulted in an intense phosphorescence.

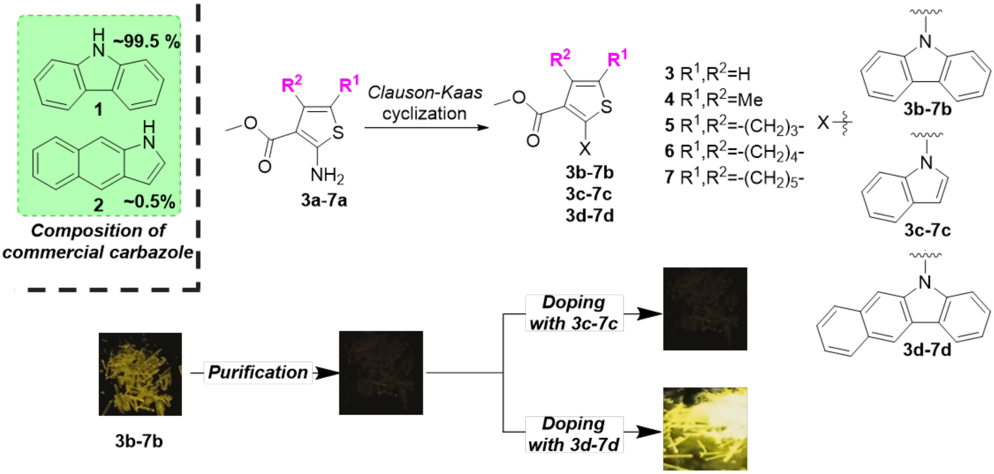


Fig. Impurity-induced phosphorescence in carbazoles **3b**–**7b**.

References

[1] Zhao, W.; He, Z.; Lam, J.W.Y.; Peng, Q.; Ma, H.; Shuai, Z.; Bai, G.; Hao, J.; Tang, B.Z. *Chem.* **2016**, *1*, 592–602.

[2] Chen, C.; Chi, Z.; Chong, K.C.; Batsanov, A.S.; Yang, Z.; Mao, Z.; Yang, Z.; Liu, B. *Nat. Mater*. **2020**, *20*, 175–180.

SYNTHESIS AND USE OF NOVEL MOLECULARLY IMPRINTED POLYMERS FOR SELECTIVE EXTRACTION OF CATECHOLAMINES AND THEIR METABOLITES

Artūrs Šilaks, Antons Podjava

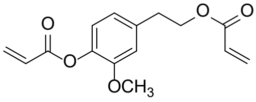
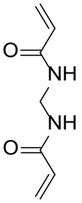
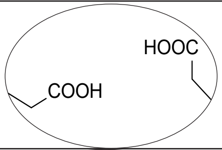
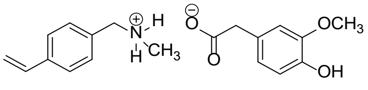
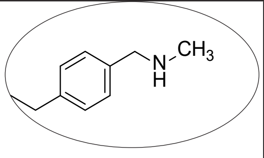
Laboratory of Chromatography and Mass Spectrometry, Faculty of Chemistry,
University of Latvia, Jelgavas str. 1, Riga, Latvia.
E-mail: asilaks@gmail.com

Catecholamines (CAs) are important hormones and neurotransmitters. Abnormal levels of CAs in bodily fluids can be associated with neurodegenerative diseases as well as adrenogenic tumors. Simultaneous determination of CAs and their metabolites in biological fluids is an efficient way of diagnosis and treatment of the aforementioned diseases. Molecularly imprinted polymers (MIPs) are slowly replacing conventional sorbents used in solid-phase extraction (SPE) to achieve superior selectivity for target analyte isolation from complicated matrices. So far there were no attempts to obtain selective sorbents for simultaneous isolation of CAs and their metabolites except the one made by our group [1].

To provide enhanced aqueous stability for polymer particles and improve molecular recognition for both CAs and their metabolites, the MIP is synthesized using methylenebisacrylamide (MBAA, cross-linker, **4**) with acrylated homovanillic alcohol (HVAAC, **1**), *N*-(4-vinylbenzyl)-*N*-methylamine (NVNM, **2**) and homovanillic acid (HVA, **3**) that act as templates/monomers for CAs and their metabolites, respectively.

MIP sorbents and non-imprinted polymers (NIPs) with varied cross-linker/monomer ratios were prepared and packed into cartridges. Standard analyte mixture was passed through. The imprinting factor (IF), selectivity factor and recovery for each compound were compared to the corresponding NIPs. The preliminary results show that the MIPs have improved retention of CAs compared to NIPs (pH 6). The best-performing MIP will be chosen for further studies.

Table. Structural formulas of the compounds chosen for synthesis of the MIPs.

	Combined Functional Monomer/Template	**Cross-linker**	**Binding Site Functionality**
CAs, MN and NM	 1	 4	
HVA and VMA	 2 3 (NVNM/HVA salt)		

Reference

[1] Podjava, A.; Šilaks, A. *J. Liq. Chromatogr. Relat. Technol.* **2021**, *44*, 181–188.

Acknowledgement. This work is supported by the Fundamental and Applied Research Project lzp-2022/1-0141.

Section of
Institute of Chemical Physics

ANALYSIS OF LATVIAN DARKHEAD SHEEP WOOL FIBERS FOR APPLICATION IN AIR FILTRATING SYSTEMS

Nadīna Tīna Vanaga[1, 2], Līga Avotiņa[1], Arturs Zariņš[1, 2], Gunta Ķizāne[1]

[1] *Institute of Chemical Physics, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[2] *Faculty of Natural Sciences and Mathematics, Daugavpils University, Parades str. 1, Daugavpils, Latvia*
E-mail: nadina.vanaga@outlook.com

Latvian Darkhead (LD) is a local origin sheep breed in Latvia. There are publications devoted to the development of this breed [1, 2]. However, only recently an interest about application of the LD sheep wool to various sustainable applications, has been expanded. Among the possible applications is an incorporation of wool fibers into the air filtrating specimens. However, fresh-cut wool contains impurities, that may affect the performance of the fibers. Therefore, carding is suggested as fiber preparation method. In present work a comparison of chemical bonds of carded and non-carded wool is performed. Chemical bonds of sheep wool fibers were analysed and compared by means of Fourier transform infrared (FTIR) spectrometry and sorption efficiency of volatile gaseous compounds is tested.

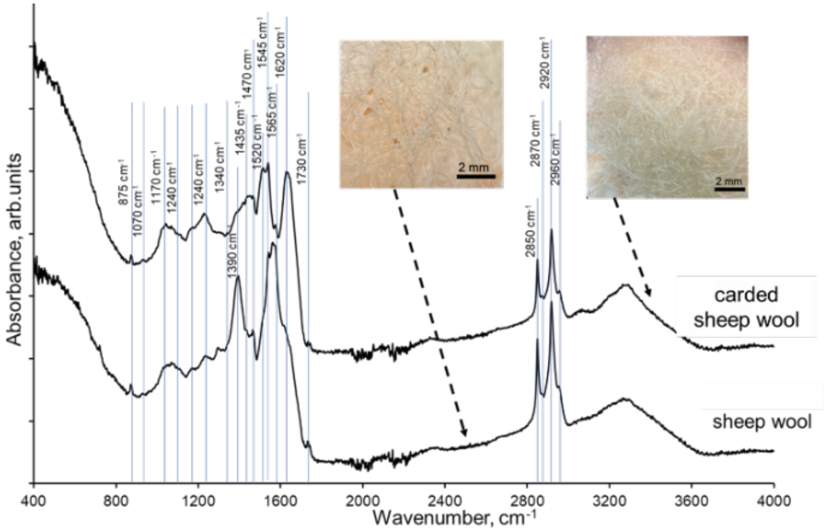


Fig. FTIR spectra of LD sheep wool and carded wool.

FTIR analysis shows, that in the spectra of pre-treated wool intensities of signals at 1390 and 1620 cm^{-1} have been changed, corresponding to the -OH and C=O containing bonds [3]. The spectrum of pre-treated sheep wool further is used as reference spectrum for analysis of absorbed compounds.

References

[1] Sjakste, T.; Paramonova, N.; Grislis, Z.; Trapina, I.; Kairisa, D. *DNA and Cell Biology.* **2011**, *30*, 433–444.

[2] Bārzdina, D.; Kairisa, D. *Animal Production, Animal Welfare and Protection of Animal Health.* **2015**, 361–366.

[3] Dayioglu, H.; Kut, D.; Merdan, N.; Canbolat, S. *Procedia Soc. Behav. Sci.* **2015**, *195*, 1609–1617.

Acknowledgement. Research performed within the European Regional Development Fund (ERDF) 1.1.1.1 Practical Orientation Research 4th round project No. 1.1.1.1/20/A/155 “Development of novel and innovative composite materials with enhanced sorption properties from renewable biological natural resources available in the Republic of Latvia for commercial air purification filtration systems”.

INFLUENCE OF FABRICATION RELATED EFFECTS ON THE LUMINISCENCE PROPERTIES OF LITHIUM ORTHOSILICATE AND LITHIUM METATITANATE TWO-COMPONENT MATERIAL

Mareks Seņko[1, 2], **Artūrs Zariņš**[1, 3], **Aija Trimdale-Deksne**[2],
Aleksandrs Dutovs[1], **Raimonds Meija**[1], **Juris Prikulis**[1], **Gunta Ķizāne**[1]

[1] *Institute of Chemical Physics, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[2] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[3] *Faculty of Natural Sciences and Mathematics, Daugavpils University, Parades str. 1A, Daugavpils, Latvia*
E-mail: mareks.senko@lu.lv

Lithium orthosilicate (Li_4SiO_4) is one of the lithium containing compounds, which is extensively studied for various application purposes, e.g., in future thermonuclear fusion reactors to generate tritium breeding due to the high melting point, high lithium density acceptable tritium release behaviour, and good radiation stability [1], and as solid sorbent for carbon dioxide capture due to its high sorption capacity and cyclic stability [2]. Advanced ceramic breeder pebbles consisting of 65 mol% Li_4SiO_4 and 35 mol% lithium metatitanate (Li_2TiO_3) are considered as the most promising candidate material for tritium breeding, due to improved mechanical properties in comparison to single-phase Li_4SiO_4 ceramic pebbles [3].

Objectives of this study include photoluminescence (PL) measurements for possible characterization of intrinsic and extrinsic defects in Li_4SiO_4-Li_2TiO_3 two-component material, prepared using different fabrication approaches, solvents, and chelating reagents. The Li_4SiO_4-Li_2TiO_3 powder samples were prepared using low-cost solid-state synthesis method, solution-based sol-gel method, and by mechanically mixing prepared single-phase components. The prepared powder samples were pressed into pellets using a manual hydraulic press.

The obtained results of powder X-ray diffractometry (p-XRD) showed that the prepared powder samples using all three fabrication approaches contain similar crystalline phases – monoclinic Li_4SiO_4 and monoclinic Li_2TiO_3. The surface microstructure and chemical composition of the pressed pellets were investigated using scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDX). The pellets have two main PL band groups at room temperature: (1) in the blue-light region (430–460 nm) and (2) in the red-light region (680–740 nm) related to intrinsic defects in both crystalline phases. The prepared samples via solid-state synthesis and sol-gel route have more intensive luminescence in blue light region, while luminescence in samples prepared by mechanical mixing both components dominate in red light region.

References

[1] Knitter, R.; Kolb, M.H.H.; Kaufmann, U.; Goraieb, A.A. *J. Nucl. Mater.* **2013**, *442*, S433–S436.

[2] Wang, K.; Li, W.; Yin, Z.; Zhou, Z.; Zhao, P. *Energy & Fuels*. **2017**, S6257–S6265.

[3] Boccaccini, L.V.; Arbeiter, F.; Arena, P.; Aubert, J.; Bühler, L.; Cristescu, I.; Del Nevo, A.; Eboli, M.; Forest, L.; Harrington, C.; Hernandez, F. *Fusion Engineering and Design*. **2022**, *179*, 113–116.

Acknowledgement. This research has been performed within the framework of project "Implementation of activities described in the Roadmap to Fusion during Horizon Europe through a Joint Programme of the members of the EUROfusion consortium under Horizon Europe" (project agreement No. 101052200).

MASS-SEPARATION OF ^{44,47}SC RADIONUCLIDES AT THE CERN-MEDICIS FACILITY

Edgars Mamis[1, 2], Cyril Bernerd[1, 3], Eric Chevallay[1], Bernard Crepieux[1], Charlotte Duchemin[1], Patrīcija Kalniņa[2], Qaiser Khan[4], Laura Lambert[1], Elīna Pajuste[1, 2], Maija Radziņa[5], Ralf Rossel[1], Sebastian Rothe[1], Thierry Stora[1]

[1] CERN, Esplanades des Particules 1, 1211 Meyrin, Geneva, Switzerland
[2] Institute of Chemical Physics, University of Latvia, Jelgavas str. 1, Riga, Latvia
[3] KU Leuven, Institute for Nuclear and Radiation Physics,
Celestijnenlaan 200d, 3001, Leuven, Belgium
[4] Pakistan Atomic Energy Commission, Near K-Block, P.O. Box 1114, Islamabad, Pakistan
[5] Faculty of Medicine, University of Latvia, 3 Jelgavas str., Riga, Latvia
E-mail: edgars.mamis@cern.ch; edgars.mamis@lu.lv

The CERN-MEDICIS facility specializes in extraction and purification by mass-separation of a wide range of novel medical radionuclides, produced in nuclear reactions resulting from 1.4 GeV protons from the CERN Proton Synchroton Booster (PSB) impinging on thick targets. Another mode of operation utilizes externally irradiated samples in nuclear reactors or by cyclotrons [1]. Due to its unique capabilities and role in translational research by providing novel medical radionuclides, CERN-MEDICIS has triggered the PRISMAP (Production of high purity isotopes by mass separation) consortium of members 13 countries that aims to provide a sustainable source of high purity grade novel radionuclides for medical research and create a single-entry point for all researchers and users active in this field [2].

The mass-separated radionuclides are most often delivered in the form of singly charged atomic ions, but with development of target materials and more versatile and selective ion sources, more refractory or exotic radionuclides in the form of molecular species could be successfully extracted [3]. Molecules have been studied to efficiently deliver ion beams of release-limited elements such as Y, Zr, Mo, W, Ti, V as well as medical ^{43,44m,44g,47}Sc radionuclides which are ideal for “matched theranostic pair” radiopharmaceutical development for cancer treatment [3–5]. The use of molecular beams for extraction is motivated by the significantly higher volatility resulting in improved efficiencies, as well as higher radionuclide purity. Extracting radionuclides on a molecular sideband shifts the mass of interest and can be used as a technique to improve radioactive ion beam purity by choosing to collect on a mass with minimal isobar contamination [5–6].

Natural titanium and vanadium targets were irradiated with the 1.4 GeV protons delivered at ISOLDE to produce Sc isotopes for mass-separation at CERN-MEDICIS. The presence of long-lived contaminant isotopes such as ^{46}Sc ($t_{1/2}$ = 83,8 d) in radiolabelling with radiopharmaceuticals is not acceptable, therefore the Sc radionuclide mass-separation step is mandatory.

Extraction of Sc radionuclides as halide molecular beams was studied with a Versatile Arc Discharge Ion Source (VADIS) target unit. Nevertheless, chemical purification step must be added to remove isobaric contaminants. Ion exchange chromatography with DGA resin was studied to chemically purify the collected medical Sc radionuclides.

References

[1] Duchemin, C.; Ramos, J.P.; Stora, T. et al., CERN-MEDICIS collaboration. *Front. Med.* **2021**, *8*, 693682.

[2] www.prismap.eu (This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 101008571.)

[3] Ballof, J.; Chrysalidis, K.; Düllmann, C.; Fedosseev, V.; Granados, E.; Leimbach, D.; Marsh, B.; Ramos, J.P.; Ringvall, M.A.; Rothe, S.; Stora, T.; Wilkins, S.; Yakushev, A. *Eur. Phys. J. A.* **2022**, *58*.

[4] Hoff, P.; Jonsson, O.C.; Kugler, E.; Ravn, H.L. *Nucl. Instrum. Methods Phys. Res.* **1984**, *221*(2), 313–329.

[5] Kronenberg, A.; Spejewski, E.H.; Carter, H.K.; Mervin, B.; Jost, C.; Stracener, D.W.; Lapi, S.; Bray, T. *Nucl. Instrum. Methods Phys. Res. B.* **2008**, *266*(19–20), 4252–4256.

[6] Eder, R.; Grawe, H.; Hageb, E.; Hoff, P.; Kugler, E.; Ravn, H.L.; Steffensen, K. *Nucl. Instrum. Methods Phys. Res. B.* **1992**, *B-62*, 535–540.

Acknowledgements. This work was supported in part by Latvian Council of Science, grant number: lzp-2021/1-0539 "Novel and efficient approach of medical 43Sc, 44Sc and 47Sc radionuclide separation and purification from irradiated metallic targets towards radiopharmaceutical development for theranostics" as well as the European Union's Horizon 2020 research and innovation programme under grant agreement No. 101008571 (PRISMAP – The European medical radionuclides programme).

POLYMER ELECTROLYTE MEMBRANE EFFECT ON WATER ELECTROLYSIS HYDROGEN GENERATION FARADAIC EFFICIENCY

Matīss Sondars, Rūdolfs Jānis Zabolockis, Elīna Pajuste
Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia
Institute of Chemical Physics, University of Latvia, Jelgavas str. 1, Riga, Latvia
E-mail: matiss.sondars@lu.lv

Polymer electrolyte membrane (PEM) water electrolysis is being used for generating hydrogen from water, main advantages include producing hydrogen and oxygen with high purity, it operates at room temperature, electrolysis can be safely performed with higher current densities. In electrolysis different polymer electrolyte membranes are used and hydrogen generation Faradaic efficiency is one of parameters that indicates membrane quality and suitability for water electrolysis.

In this work hydrogen generation Faradaic efficiencies were determined with 8 different polymer electrolyte membranes:

1. SPEEK (sulfonated poly (ether ether ketone)) with 3 different degrees of sulfonation (0,7; 0,77; 0,9);
2. Nafion 212;
3. SPEEK (DS = 0,77) and Nafion 212 without graphene coating;
4. SPEEK (DS = 0,7; 0,9) irradiated with accelerated electron beam (500 kGy, E ~ 10 MeV).

Highest hydrogen generation Faradaic efficiency was determined to be for electron beam irradiated SPEEK with degree of sulfonation 0,9 (η_F = 100,2 ± 0,6%) (Fig.). The lowest hydrogen generation Faradaic efficiency was determined for SPEEK membrane with degree of sulfonation 0,7 (η_F = 86,3 ± 1,7%).

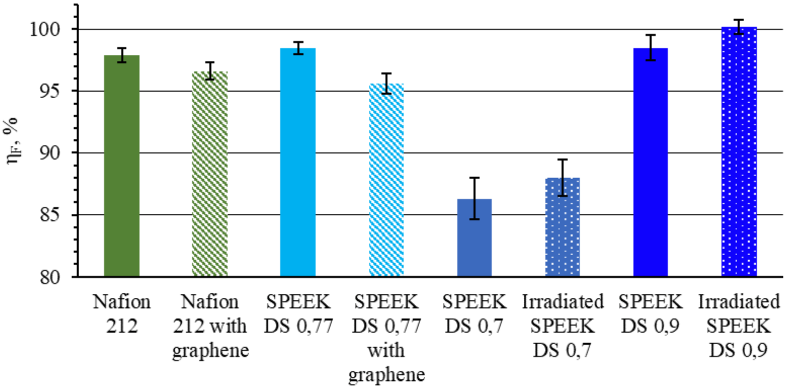


Fig. Hydrogen generation Faradaic efficiency dependence on used PEM in water electrolysis.

Acknowledgement. This research has been performed within the framework of the European Regional Development Fund (ERDF) project No. 1.1.1.1/19/A/137.

TRITIUM ACCUMULATION IN JET ITER-LIKE-WALL COMPOSITE MATERIALS FROM DIVERTOR TILES

Annija Elizabete Goldmane[1, 2], Anete Stīne Teimane[1, 2], Elīna Pajuste[2], Līga Avotiņa[2]

[1] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[2] *Institute of Chemical Physics, University of Latvia, Jelgavas str. 1, Riga, Latvia*
E-mail: annija_elizabete.goldmane@lu.lv

In recent years, there has been a growing interest in plasma facing materials research for application in nuclear fusion. The ITER (International Thermonuclear Experimental Reactor) – Like-Wall project has been carried out at the Joint European Torus (JET) to test plasma facing materials relevant to ITER [1]. Tungsten (W) coated carbon fibre reinforced graphite composites (CFC) are exploited in present fusion devices like JET. It is already known that CFC accumulation of radioactive hydrogen isotope tritium (used as nuclear fuel in fusion) is significant, an understanding of tritium release mechanism is required in order to estimate tritium accumulation and decontamination possibilities [2].

Assessment of the total amount of tritium accumulated in the materials is important from the point of view of radiation safety and economy, because it mostly remains on the surface of the material, although as an isotope of hydrogen, it can be quite mobile and can diffuse deeper in bulk as well as energetic ion implantation could take place [3]. Trapping of deuterium at W/Mo interfaces has been studied by number of authors [4]. Tritium accumulation and release properties depend on the location of the wall components in the vacuum vessel, conditions of exposure to plasma and to the material itself [1, 5].

W/Mo coated CFC tiles from the JET divertor exposed during operational campaigns 2011–2016, were analyzed by Thermal Desorption spectrometry (TDS), full combustion, scanning electron microscopy (SEM) in combination with energy dispersive X-ray spectroscopy. Tritium desorption performed in the Ar + 0.1% H_2 gas flow and measured by tritium monitor TEM 2102A [1]. Tritium results were compared with the thickness of the deposited layer measured on the plasma facing surface of the samples.

Desorption spectra as well as SEM imaging for surface morphology gives information about the tritium distribution tendencies in the vacuum vessel. Obtained results will be used for developing recommendations for tritium release techniques from plasma exposed materials.

References

[1] Pajuste, E.; Teimane, A.S.; Kizane, G.; Avotina, L.; Halitovs, M.; Lescinskis, A.; Vitins, A.; Kalnina, P.; Lagzdina, E.; Zabolockis, R.J. *Phys. Scr.* **2021**, *96*(12), 124050.

[2] Joffrin, E. et al. *Nucl. Fusion.* **2019**, *59*(11), 112021.

[3] Tobita, K.; Nishio, S.; Konishi, S.; Sato, M.; Tanabe, T.; Masaki, K.; Miya, N. *Fusion Eng. Des.* **2003**, *65*(4), 561–568.

[4] Bergsåker, H.; Bykov, I.; Zhou, Y.; Petersson, P.; Possnert, G.; Likonen, J.; Pettersson, J.; Koivuranta, S.; Widdowson, A.M.; JET contributors. *Phys. Scr.* **2016**, *T167*, 014061.

[5] Coad, J.P.; Rubel, M.; Likonen, J.; Bekris, N.; Brezinsek, S.; Matthews, G.F.; Mayer, M.; Widdowson, A.M. *Fusion Eng. Des.* **2019**, *138*, 78–108.

INFLUENCE OF AIR HUMIDITY ON CHEMISORBTION PROCESSES OF CARBON DIOXIDE IN LITHIUM ORTHOSILICATE CONTAINING CERAMICS

Anna Ansone[1,2], Inita Putniņa[3], Mareks Seņko[1,2], Artūrs Zariņš[1,4], Līga Avotiņa[1], Artis Kons[2], Kristaps Saršūns[2], Gunta Ķizāne[1,2]

[1] *Institute of Chemical Physics, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[2] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[3] *Iecavas secondary school, Skolas str. 37, Iecava, Latvia*
[4] *Faculty of Natural Sciences and Mathematics, Daugavpils University, Parades str. 1A, Daugavpils, Latvia*
E-mail: anna.ansone@lu.lv

Lithium orthosilicate (Li_4SiO_4) containing ceramics are being developed for use in thermonuclear fusion reactors as potential solid-state materials for tritium breeding [1]. Li_4SiO_4 undergoes various chemisorption processes while exposed to atmospheric air, which contains carbon dioxide (CO_2) and water (H_2O) vapour, and forms various chemisorption products, including lithium carbonate (Li_2CO_3) and lithium hydroxide (LiOH), on the sample surface. Formation of chemisorption products on a sample surface could affect the radiation-induced processes, analysis of the irradiated samples, and correct interpretation of the obtained results.

In this study, long-term experiment was performed in order to investigate influence of humidity on the formation of chemisorption products in air atmosphere. Pressed Li_4SiO_4 pellets with a diameter of 10 mm have been held in air atmosphere with three different relative humidities (RH) up to 118 days. The changes of surface chemical composition and the effect of storage atmosphere has been investigated using attenuated total reflectance – Fourier transform infrared (ATR FTIR) spectrometry. The mass of chemisorbed gaseous compounds has been determined using gravimetry, while the desorption processes of chemisorbed CO_2 and H_2O has been analysed using thermogravimetry/differential scanning calorimetry (TG/DSC).

The obtained data of gravimetry method showed weight gain for Li_4SiO_4 samples held in low, average and high humidity atmosphere. It is significantly higher (up to 58 wt.%) for the Li_4SiO_4 which was held in air atmosphere with a high humidity (RH = 68–77%) in comparison to the pellets held in air atmosphere with an average humidity (RH = 21–37%) – up to 3 wt.% and a low humidity (RH = 12–20%) – up to 2 wt.%. ATR-FTIR spectrometry confirmed the presence of Li_2CO_3 on the surface of all samples held in different air humidity. TG/DSC method indicated at least two main release stages of gaseous compounds and sample weight loss up to 49%. Based on the obtained results, it is concluded that the formation of Li_2CO_3 on the pellet surface is directly related to air humidity. For further irradiation experiments with various radiation types, it can be recommended to store Li_4SiO_4 containing ceramics in atmosphere free of H_2O vapour and CO_2 in order to prevent the chemisorption processes and the formation of Li_2CO_3 and other chemisorption products. Li_4SiO_4 containing ceramic materials should also be thermally pre-treated at temperature up to 900 °C to desorb all chemisorbed gaseous compounds before irradiation experiments.

Reference

[1] Boccaccini, L.V.; Arbeiter, F.; Arena, P.; Aubert, J.; Bühler, L.; Cristescu, I.; Del Nevo, A.; Eboli, M.; Forest, L.; Harrington, C.; Hernandez, F.; Knitter, R.; Neuberger, H.; Rapisarda, D.; Sardain, P.; Spagnuolo, G.A.; Utili Vala, L.; Venturini, A.; Vladimirov, P.; Zhou, G. *Fusion Engineering and Design*. **2022**, *179*, 113116.

AUTOMATED SPECTROGRAM ACQUISITION WITH AUXILIARY MEASUREMENTS FOR CHARACTERIZATION OF OPTICAL SENSOR SUBSTRATES

**Oskars Putāns, Amanda Reķe, Uldis Malinovskis, Aleksandrs Dutovs,
Raimonds Popļausks, Irina Oliševeca, Donāts Erts, Juris Prikulis**

Institute of Chemical Physics, University of Latvia, Jelgavas str. 1, Riga, Latvia
E-mail: oskars.putans@lu.lv

A new type of optical sensors, consisting of bulk Al surface, sub-wavelength layer of porous anodic aluminum oxide (PAAO), and a layer of Au nanoparticles (AuNP) was recently developed [1]. The AuNPs support localized surface plasmon resonances (LSPR) that are sensitive to changes of the refractive index, which can be useful in biosensing applications. The LSPR sensitivity for Al-PAAO-Au systems can be optimized by careful selection of geometric parameters, such as PAAO layer thickness and AuNP size. However, the substrate morphology is subject to production tolerances. In order to reach conclusive results, the samples need to be verified before biosensing experiments. To increase data filtering efficiency, multiple instruments could be used simultaneously for rapid substrate characterization. However, even modern research equipment often uses custom or legacy programming interfaces. Sometimes instrument manufacturers provide only graphical user interface, designed for human operators.

In order to integrate the available equipment in an automated system we have created a modular software, which is capable of taking multiple high-speed measurements. The central server controls the spectrometer and microscope stage. It provides an IoT (internet of things) network for programs and devices capable of simultaneously reading instrument data and storing it in an organized fashion for easier data analysis. All of the current programs utilize Python 3.11 or 2.7, however, software written in any programming language capable of communication through TCP/IP (Transmission Control Protocol/Internet Protocol) can be added to the network. Communication is built on a lightweight publishing-subscribing protocol utilizing TCP connections, which allow the server to give custom commands and updates to other programs, while allowing it to be read and parsed by other software. Because the only requirement is a network connection, any device with TCP/IP functionality can connect to the automated system. Every new instrument has to be adapted to provide an interface to ensure proper interaction with the server. The server is the main authority taking readings at specific points of the sample and responsible for the most time-consuming measurements. To ensure rapid experiments, clients have no authority over delaying the server's processes, sacrificing auxiliary data integrity for increased data collection speed, and prevention of faulty clients halting the entire experiment. Thus, should any instrument or program apart from the server fail, the rest of the network has no issue ignoring the faulty endpoint.

The software system was successfully used to characterize Al-PAAO-Au films in reflection and scattering modes for interferometric and LSPR plasmonic sensing.

Reference

[1] Malinovskis, U.; Popļausks, R.; Jurkevičiūté, A.; Dutovs, A.; Berzins, K.; Perkanuks, V.; Simka, W.; Muiznieks, I.; Erts, D.; Prikulis, J. *ACS Omega*. **2022**, *7*, 40324–40332.

CHEMICAL SEPARATION AND PURIFICATION OF STABLE ^{45}SC FROM CERN-MEDICIS MASS-SEPARATOR COLLECTION FOILS

Patrīcija Kalniņa[1, 2], Edgars Mamis[1, 2, 3], Laura Lambert[3], Qaiser Khan[3, 4], Elīna Pajuste[1, 2], Thierry Stora[3]

[1] *Institute of Chemical Physics, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[2] *Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[3] *CERN, Espl. des Particules 1, Meyrin, Switzerland*
[4] *Pakistan Atomic Energy Commision, Near K-Block, P.O. Box 1114, Islambad, Pakistan*
E-mail: patricija.kalnina@lu.lv

Certain radionuclides of the chemical element Scandium are promising candidates to be used for radionuclide targeted therapy and positron emission tomography (PET/CT). ^{44}Sc or ^{43}Sc can be used for diagnostic imaging purposes and monitoring therapy response and ^{47}Sc for therapeutic purposes or SPECT diagnostics [1].

CERN MEDICIS produces medical radionuclides by recovering the 1.4 proton beam from CERN-PSB before it reaches the beam dump using thick targets placed behind the ISOLDE targets. These radionuclides are then extracted and separated according to their atomic mass via MEDICIS mass-separator and implanted in a Zinc or Aluminium covered gold or salt covered aluminium foils [2]. After collecting the radionuclides on the foil, radiochemical manipulations are necessary to remove isobaric (equal mass) impurities.

Ion exchange chromatography is one of the most powerful and widely used methods for radiochemical separations. With a proper choice of conditions, ion exchange is very useful for separating carrier-free radionuclides from a bulk target having a significantly lower affinity toward the resin [3].

A method for stable Scandium separation from Zinc and Aluminium standard solutions was developed using DGA resin. ICP-MS analyses were performed on each of the collected samples to determine the concentration of zinc, aluminium, and scandium ions. Two resins (DGA normal and DGA branched) were compared to determine the most appropriate resin for Scandium separation.

In this method DGA resin trapped more than 90% of the total Scandium ions present in the stock solution. This method was then applied to the separation of stable scandium from CERN MEDICIS mass – separator collection foils with Aluminium coating (500 nm). As it is planned to implant Sc on Al coated gold foils in the future, separation of scandium from Al/Au foil was performed.

References

[1] Loveless, S.C.; Blanco, J.R.; Diehl III, G.L.; Elbahrawi, R.T.; Carzaniga, T.S.; Braccini, S.; Lapi, S.E. *J. Nucl. Med.* **2021**, *62*(1), 131–136.

[2] Duchemin, C.; Ramos, J.P.; Stora, T., MEDICIS collaboration board. CERN MEDICIS: A Unique Facility for the Production of Non-conventional Radionuclides for the Medical Research. 11th International Particle Accelerator Conference, Caen-France, **2020**.

[3] Glueckauf, E. *J. Am. Chem. Soc.* **1959**, *81*(19), 5262–5263.

Acknowledgement. Project No. lzp-2021/1-0539 “Novel and efficient approach of medical ^{43}Sc, ^{44}Sc and ^{47}Sc radionuclide separation and purification from irradiated metallic targets towards radiopharmaceutical development for theranostics”.

FABRICATION AND ENCAPSULATION OF POLYCRYSTALLINE ZNO NANOWIRE NETWORKS FOR USE IN THERMOELECTRIC GENERATORS

Raitis Sondors, Margarita Baitimirova, Donāts Erts, Jana Andžāne

Institute of Chemical Physics, University of Latvia, Jelgavas str. 1, Riga, Latvia
E-mail: raitis.sondors@lu.lv

Almost half of the final energy consumption in the EU is used for heating and cooling, of which 80% accounts for buildings [1]. This power consumption could be significantly reduced by capturing and converting domestic waste heat to electricity using thermoelectric (TE) materials. Typical high-performance TE materials, such as Bi_2Te_3, Bi_2Se_3, SnSe and PbTe, among others, are expensive, environmentally toxic, scarce, and easily oxidized, diminishing their TE properties [2]. Significant efforts have been devoted to developing environmentally friendly oxide based TE materials, fabricated from cheap, widely available materials. ZnO has been reported as a potential TE material with a high Seebeck coefficient [3]. The TE properties of ZnO can potentially be further improved using nanostructuring.

In this work, polycrystalline ZnO nanowire (NW) networks have been fabricated by oxidizing Zn NW networks obtained by physical vapor deposition on glass substrates (Fig.). The ZnO NW networks were encapsulated in commercially available epoxy glue. Their morphology was characterised via scanning electron microscopy (SEM). Their electric and TE properties were measured with a custom made setup before and after encapsulation. Analysis of the measured properties shows that ZnO nanowire networks are promising materials for use in TE generators.

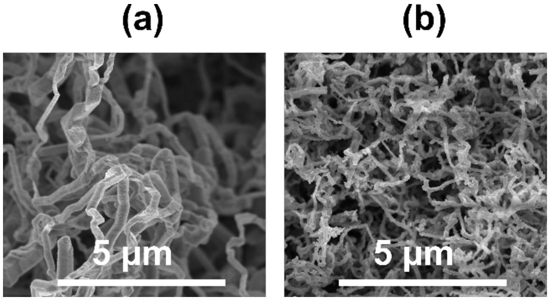


Fig. SEM images: (a) Zn nanowire networks, fabricated by physical vapor deposition; (b) ZnO nanowire networks, obtained by oxidizing Zn nanowire networks.

References

[1] Directive 2018/844 of the European Parliament and of the Council. *OJEU*. **2018**, *L 156*, 75–91, ELI: http://data.europa.eu/eli/dir/2018/844/oj

[2] Lwin, M.L.; Dharmaiah, P.; Madavali, B.; Lee, C.H.; Shin, D. won; Song, G.; Lee, K.H.; Hong, S.J. *Intermetallics.* **2018**, *103*, 23–32.

[3] Zappa, D.; Dalola, S.; Faglia, G.; Comini, E.; Ferroni, M.; Soldano, C.; Ferrari, V.; Sberveglieri, G. *Beilstein J. Nanotechnol.* **2014**, *5*, 927–936.

THERMOELECTRIC PROPERTIES OF ENCAPSULATED COPPER OXIDE NANOWIRE NETWORKS

Davis Gavars[1], Raitis Sondors[1], Anatolijs Sarakovskis[2], Donāts Erts[1], Jana Andžāne[1]

[1] Institute of Chemical Physics, University of Latvia, Jelgavas str. 1, Riga, Latvia
[2] Institute of Solid State Physics, University of Latvia, Kengaraga str. 8, Riga, Latvia
E-mail: davis.gavars@lu.lv

Both cupric oxide (CuO) and cuprous oxide (Cu2O) have been investigated for applications in catalysis [1], sensors [2], supercapacitors [3], etc. Thermoelectric properties of copper oxides have also been researched and show promising results for the potential use in thermoelectric generators (TEG). Most commercially available TEGs consist of Bi2Se3. To utilize TEGs domestically or as part of a wearable device, copper oxides would be preferable in their manufacture, because they are less toxic and less harmful to the environment [4]. In order to utilize copper oxides as thermoelectric materials in TEGs, appropriate encapsulation methods must be developed, such that preserve or enhance the thermoelectric properties.

In this work, CuO nanowires were synthesised by thermal oxidation of copper foil and annealed in a vacuum to produce Cu2O nanowires [4]. Nanowire networks on a glass substrate were fabricated using the drop-coating method. The prepared nanowire networks were further encapsulated in different polymers and their thermoelectric and electric properties were compared. Morphology of the nanowires and prepared nanowire networks was characterized using scanning electron microscopy (SEM). The crystalline structure of nanowires was characterized using X-ray diffraction spectroscopy (XRD). Elemental composition and chemical state of the copper atoms in the nanowires was characterized using X-ray photoelectron spectroscopy (XPS). Electrical and thermoelectric properties of the nanowire networks were measured using Keithley 6430 sourcemeter and HP 34401A multimeter. The effect of encapsulation on the thermoelectric and electric properties of Cu2O nanowire networks was investigated.

References

[1] Scuderi, V.; Amiard, G.; Boninelli, S.; Scalese, S.; Miritello, M.; Sberna, P.M.; Impellizzeri, G.; Privitera, V. *Mater. Sci. Semicond. Process.* **2016**, *42*, 89–93.

[2] Hsu, C.L.; Tsai, J.Y.; Hsueh, T.J. *Sensors Actuators B Chem.* **2016**, *224*, 95–102.

[3] Zhao, J.; Shu, X.; Wang, Y.; Yu, C.; Zhang, J.; Cui, J.; Qin, Y.; Zheng, H.; Liu, J.; Zhang, Y.; Wu, Y. *Surf. Coatings Technol.* **2016**, *299*, 15–21.

[4] Sondors, R.; Gavars, D.; Sarakovskis, A.; Kons, A.; Buks, K.; Erts, D.; Andzane, J. *Mater. Sci. Semicond. Process.* **2023**, *159*, 107391.

INTRODUCTION OF MAGNETIC IMPURITIES INTO THE BI_2SE_3 THIN FILMS

Andrei Felsharuk, Jana Andžāne, Gunta Kunakova, Donāts Erts
Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia
E-mail: andrei.felsharuk@lu.lv

Topological insulators (TIs) are a new class of materials with an insulating bulk and topologically protected by time-reversal symmetry (TRS) conductive surface states. Breaking the TRS of TIs offers the opportunity for unique physical phenomena to emerge, which may have potential applications in future electronic devices. One of the approaches to breaking TRS is the introduction of magnetic dopants into TIs [1].

In this work, synthesis and magnetotrasport measurements of pristine and Fe-doped Bi_2Se_3 thin films are presented and discussed.

Pristine and Fe-doped Bi_2Se_3 thin films were synthesized by a simple physical vapour deposition method [2] on quartz using ferrocene in different concentrations as a dopant.

Compositional and structural analyses of synthesized nanostructures were performed using different techniques such as scanning (SEM), atomic force microscopy (AFM) as well as energy-dispersive X-ray (EDX) spectroscopy. Magnetotransport measurements of synthesized structures were performed under magnetic field from –9 T to +9 T applied perpendicularly to the sample surface.

The results of this study showed that the charge carrier mobilities of Fe-doped Bi_2Se_3 thin films are distinctly reduced in comparison with the pristine Bi_2Se_3 thin films, indicating increased disorder levels in the Bi_3Se_3 structure due to the incorporation of Fe atoms. Charge carrier densities in Fe-doped films are lower in comparison with pristine films which means that Fe atoms substitute Bi and act as acceptor causing slight change in the carrier density [2].

References

[1] Niu, W.; Du, K.; Wang, S.; Zhang, M.; Gao, M.; Chen, Y.; Liu, H.; Zhou, W.; Song, F.; Wang, P.; Xu, Y. *Nanoscale.* **2017**, *9*(34), 12372–12378.

[2] Sharma, S.; Yadav, C.S. *Physica status solidi (b).* **2020**, *257*(9), 2000086.

MODLULAR AND FLEXIBLE P-TYPE THERMOELECTRIC FILMS BASED ON ANTIMONY(III) TELLURIDE AND CNT HYBRID STRUCTURES

Elmārs Spalva[1, 2], Krišjānis Buks[1, 2], Jana Andžāne[2], Loreta Brauna[2], Donāts Erts[2]

[1] *SIA 3D Strong, Institūta str. 36, Ulbroka, Latvia*
[2] *Institute of Chemical Physics, University of Latvia, Jelgavas str. 1, Riga, Latvia*
E-mail: elmars.spalva@lu.lv

Use of thermoelectric generators (TEGs) is the most direct way of capturing waste heat by converting heat-flow to electrical current. It allows for higher efficiencies for electrical devices as well as powering their own devices from potentially non-electrical heat sources, such as drainpipes, smokestacks, engines and even human skin, paving the way for self-sustained wearable electronic devices. Unfortunately, current commercially available TEGs are blockish, rigid and quite brittle, limiting their use-cases, thus, a flexible TEG is needed for allowing most configurations.

Bismuth and antimony chalcogenides are known to be one of the best high-performance thermoelectric (TE) materials for near room temperature applications. However, on their own, their mechanical properties limit their usability in flexible generators. On the other hand, organic polymers are flexible, but with poor TE performance. Combining the p-type antimony (III) telluride (Sb_2Te_3) with p-type carbon nanotubes (CNTs) allows for increased electrical conductivity and lower thermal conductivity, making conversion to electricity more effective than each material in raw form. Mechanical stability, isolation from environment and flexibility can be achieved by encapsulating a thin-film of Sb_2Te_3-CNT hybrid structures with polymers. Non electrically conductive polymers are more favorable than conductive polymers due to better chemical stability, lower toxicity and cost [1].

In this work polydimethylsiloxane (PDMS) was used as the polymer for encapsulating Sb_2Te_3-CNT hybrid structures. P-type MWCNTs were deposited onto a glass-substrate on which Sb_2Te_3 nanostructures were synthesized via a catalyst-free vapour-solid deposition method [2]. After encapsulation of the samples, two modified prototyping wires per sample with both male and female connections were bonded to the hybrid structure side of the sample using a conductive epoxy. These wire connectors allow to create widely customizable TEG circuits for application of choice. TE properties were measured using a desktop multimeter, laboratory-made heater, thermocouples and picoammeter. Resultant flexible films were characterized in different circuit configurations, measuring voltage drop across series potentiometer, with their n-type counterparts prepared as in our previous research [2] and encapsulated in PDMS in a similar manner.

References

[1] Buks, K.; Andzane, J.; Smits, K.; Zicans, J.; Bitenieks, J.; Zarins, A.; Erts, D. *Mater. Today Energy.* **2020**, *18*, 100526.

[2] Buks, K.; Andzane, J.; Bugovecka, L.; Katkov, M.; Smits, K.; Starkova, O.; Katkevics, J.; Berzins, A.; Brauna, L.; Voikiva, V.; Erts. D. *Adv. Mater. Interfaces.* **2022**, *9*, 101002.

SYNTHESIS OF TUNGSTEN DITELLURIDE NANOSTRUCTURES

Jeļena Sušinska, Gunta Kunakova

Institute of Chemical Physics, University of Latvia, Jelgavas str. 1, Riga, Latvia
E-mail: jelena.susinska@lu.lv

Tungsten ditelluride (WTe_2) has attracted significant research interest due to the largest non-saturating magnetoresistance and exotic band structure corresponding to Type-II Weyl semimetal [2], and topological surface states in certain crystallographic directions, promising for future spintronics and quantum computing applications [1–4]. However, the semimetallic nature of WTe_2 obscures access to the topological surface state transport. To study and demonstrate various fundamentally new effects originating from the surface states, WTe_2 nanostructures in the form of nanowires and nanoribbons are particularly important due to their significantly reduced number of conductance channels and increased surface to volume ratio, facilitating detection and isolation of non-trivial properties [3, 5].

In this study, the synthesis of WTe_2 nanowires was carried out by a two-step chemical vapor deposition (CVD) method, where WO_x nanowires were first obtained and then converted to WTe_2 by tellurization in an Ar/H_2 gas flow at 500–600 °C (Fig.). In both steps, synthesis parameters such as temperature, catalysts, synthesis time and pressure were adjusted to obtain nanowires with optimal W:Te stoichiometry.

The obtained nanowires will be further integrated into devices for electrical transport measurements to determine their physical properties and suitability for fundamental studies of new effects.

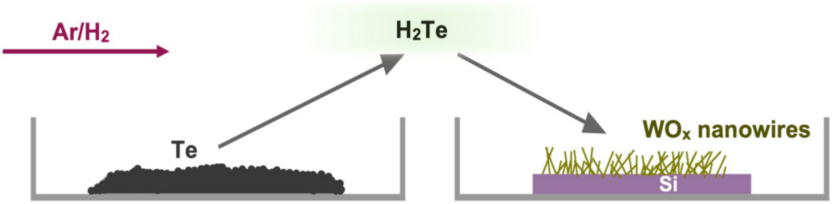


Fig. Schematic of tellurization of WO_x nanowires.

References

[1] Kane, C.L.; Mele, E.J. *Phys. Rev. Lett.* **2005**, *95*(14), 146802.
[2] Soluyanov, A.A.; Gresch, D.; Wang, Z.; Wu, Q.; Troyer, M.; Dai, X.; Bernevig, B.A. *Nature.* **2015**, *527*(7579), 495–498.
[3] Woods, J.M.; Hynek, D.; Liu, P.; Li, M.; Cha, J.J. *ACS Nano.* **2019**, *13*(6), 6455–6460.
[4] Yomogida, Y.; Nagano, M.; Hamasaki, H.; Hirahara, K.; Miyata, Y.; Yanagi, K. *Jpn. J. Appl. Phys.* **2021**, *60*(SC), SCCD02.
[5] Marra, P. *Journal of Applied Physics.* **2022**, *132*(23), 231101.

Acknowledgement. This research is funded by the Latvian Council of Science, project No. lzp-2021/1-0302.

CVD GROWTH OF WTE_2 MONOLAYERS ON INSULATING SUBSTRATES

Andrejs Terehovs[1], Anatolijs Šarakovskis[2], Gunta Kunakova[1]

[1] *Institute of Chemical Physics, University of Latvia, Jelgavas str. 1, Riga, Latvia*
[2] *Institute of Solid State Physics, University of Latvia, Ķengaraga str. 8, Riga, Latvia*
E-mail: andrejs.terehovs@lu.lv

Recent advances in two-dimensional transition metal dichalcogenide (2D-TMD) materials have attracted significant attention due to their unique electronic and optical properties [1]. Some of these materials exhibit a non-trivial topology of the electronic band structure, which leads to the emergence of exotic topological phases, such as the Type-II Weyl semimetal and Higher order topological insulator [2]. Tungsten ditelluride (WTe_2) is the most prominent 2D-TMD material hosting variety of non-trivial phases, it has been found also to exhibit a large, non-saturating magnetoresistance, making it a promising material for fundamental studies of new phenomena and for application in spintronics [2]. Chemical vapor deposition (CVD) is one of the basic methods used in the growth of 2D-TMDs. However, the CVD growth of WTe_2 with controlled thickness and coverage on SiO_2/Si substrates remains a challenge. Developing a reliable and scalable synthesis method for WTe_2 on insulating substrates (SiO_2/Si; hBN) is crucial for the investigation of electronic and optical properties, as well as for effective integration into a broad range of devices.

Here we study CVD growth parameters to controllably obtain monolayer and few-layers thick tungsten ditelluride crystals on insulating substrates. In the CVD growth, two zone furnace OTF-1200X was used. Tungsten trioxide (WO_3) and tellurium (Te) powder were placed separately in two quartz-boats in a test-tube. The precursor materials were thermally evaporated at 750–850 °C under argon and hydrogen atmosphere. The synthesized WTe_2 mono- and few layer structures were characterized using atomic force microscopy (AFM), scanning electron microscopy (SEM) as well as energy dispersive spectroscopy (XPS). The XPS showed characteristic peaks of W:Te. Additionally, optical microscopy images revealed formation of 15 to 30 micrometers large uniform and continuous WTe_2 nanosheets with a thickness of 2–5 nanometers (AFM measurements).

In this research, morphology of synthesized WTe_2 structures is found to be influenced by various synthesis conditions, including growth time, temperature, and carrier gas Ar:H_2 ratio. By identifying the optimal synthesis conditions, we are able to obtain WTe_2 nanosheets with controlled morphology.

References

[1] Choi, W.; Choudhary, N.; Han, G.; Akinwande, D.; Lee, Y.H. *Materials Today.* **2017**, *20*(3), 116–130.

[2] Huang, H.; Xu, Y.; Wang, J.; Duan, W. *WIREs Comput Mol Sci.* **2016,** *7*(4), e1296.

Acknowledgement. This research is funded by the Latvian Council of Science, project No. lzp-2021/1-0302.

ELECTROCHEMICAL TRITIUM SEPARATION USING PROTON EXCHANGE MEMBRANE ELECTROLYSIS

Rūdolfs Jānis Zabolockis, Matīss Sondars, Elīna Pajuste

Faculty of Chemistry, University of Latvia, Jelgavas str. 1, Riga, Latvia
Institute of Chemical Physics, University of Latvia, Jelgavas str. 1, Riga, Latvia
E-mail: rudolfs_janis.zabolockis@lu.lv

Tritium is a radioactive isotope of hydrogen with a half-life of 12.33 years, which occurs in nature under the influence of cosmic radiation, as well as artificially in nuclear fission processes and other nuclear chemical reactions. Tritium can be used to power thermonuclear fusion reactions, which allows energy to be produced safely and efficiently in fusion reactors such as the International Thermonuclear Fusion Reactor (ITER) therefore ways to separate it from other isotopes is of utmost importance [1]. Proton exchange membrane electrolysis is a promising method for tritium enrichment [2].

In this study, the effect of tritium-containing water (3 differing radioactivity levels) electrolysis with proton exchange membrane electrolyzer on the concentration of tritium in HTO and HT phase has been evaluated. Electrolysis has been carried out for ultrapure water containing tritium in mainly HTO form. Electrode surface area 16 cm^2, 0–2 V DC, 0–4 A DC, using commercial Nafion® 117 proton exchange membrane. The catalyst loading was 2 mg/cm^2 IrRuOx (anode) and 0,5 mg/cm^2 60% PtC (cathode). Measurement of liquid HTO water was done using liquid scintillation and of HT gas – using a tritium monitor (gas-filled detector type).

Tritium measurements were preformed and the radioactivity of both aqueous HTO and gaseous HT were determined. The isotope separation factor was calculated as the ratio between tritium and protium in gaseous to liquid phase.

References

[1] Pearson, R.J.; Antoniazzi, A.B.; Nuttall, W.J. *Fusion Engineering and Design*. **2018**, *136*, 1140–1148.
[2] Ogata, Y.; Sakuma, N.; Ohtani, N.; Kotaka, M. *Fusion Science and Technology*. **2005**, *48*, 136–139.