

Physical Chemistry



80th International Scientific
Conference of the
University of Latvia 2022

Report of Contributions

Contribution ID: 1

Type: **Oral presentation**

A new frontier for non-destructive spatial analysis of pharmaceutical solid dosage forms: micro-spatially/spatially offset low-frequency Raman spectroscopy

Friday, 11 February 2022 10:40 (15 minutes)

A non-intrusive multi-dimensional analysis method can be useful in many pharmaceutical applications, especially for the analysis of solid dosage forms, where spatial information using conventional analytical methods can typically only be obtained after destructive manipulations with samples prior to or during the measurements. This study demonstrated a new combination method of low-frequency and spatially offset Raman spectroscopy (SORS) method called spatially offset low-frequency Raman spectroscopy (SOLFERS) via the analysis of a number of model systems that showcase its capabilities for probing the layer (for example, coating) content/thickness characteristics as well as monitoring solid-state form transformations spatially.

For this purpose, celecoxib, lactose monohydrate (α -LM) and its stable anhydrous form (α -LS) as well as polyvinylpyrrolidone (PVP) were used as model compounds, and were incorporated in a variety of different multi-layer/multi-component tablets. Raman measurements were conducted using an in-house built system, and using both traditional SORS (SOLFERS) and micro-SORS (micro-SOLFERS) experimental arrangements. The associated data analysis was facilitated by the application of a variety of different chemometric techniques.

In all the explored scenarios, micro-SOLFERS/SOLFERS proved superior to the more commonly used mid-frequency (fingerprint) Raman region that is used in SORS, yielding better Raman signals from the subsurface. This aspect, for example, not only enabled a more accurate determination of surface layer (i.e., coating) thickness characteristics, but also allowed to probe much deeper subsurface areas.

Primary author: BĒRZIŅŠ, Kārlis (University of Otago, Department of Chemistry)

Co-authors: Dr FRASER-MILLER, Sara (University of Otago, Department of Chemistry); Prof. GORDON, Keith (University of Otago, Department of Chemistry)

Presenter: BĒRZIŅŠ, Kārlis (University of Otago, Department of Chemistry)

Session Classification: Physical Chemistry and Analytical Chemistry. Joint session

Track Classification: Fizikālās ķīmijas un Analītiskās ķīmijas kopējā sēde

Contribution ID: 2

Type: **Oral presentation**

Control possibilities of 2,6-dimethoxybenzoic acid conformational polymorphism using crystallization additives

Friday, 11 February 2022 14:00 (15 minutes)

University of Latvia, Faculty of Chemistry, Jēlgavas iela 1, Rīga, Latvia
e-mail: ainasemjonova@gmail.com

Active pharmaceutical ingredients (APIs) can have different physical properties (e.g., solubility [1] and bioavailability) depending on polymorph form. Many APIs have low solubility in water. Crystallization of metastable form can enhance solubility and bioavailability [2]. Unfortunately, their crystallization can be complicated due to concomitant crystallization with a stable form [3]. In this study, 2,6-dimethoxybenzoic acid (2,6-MeOBA) was used as a model substance to investigate the additive crystallization control approach. 2,6-MeOBA exists as three polymorphs. Form I form has a carboxylic group in anti-conformation, whereas forms II and III are syn-conformation [4, 5] (see Fig. 1).

Fig. 1. Relationships with 2,6-MeOBA conformations and polymorphs. The connection between forms I and III is proven in this study.

In the study, two of 2,6-MeOBA polymorphs were characterized by thermal analysis and thermodynamical stability was determined. 2,6-MeOBA was crystallized under different conditions. Water was selected for additive screening. Different molecular compounds with divergent intermolecular interaction possibilities were used as additives. The solid forms obtained in crystallization were characterized with powder X-ray diffraction.

Forms I and III are enantiotropic related. Hydroxypropyl cellulose and polyethylene glycol showed the potential to favor the formation of form III by crystallizing from water.

Acknowledgment

This work was supported within the Project identification No. 8.2.2.0/20/I/006.

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Primary author: SEMJONOVA, Aina (University of Latvia)

Co-author: BERZINS, Agris

Presenter: SEMJONOVA, Aina (University of Latvia)

Session Classification: Physical Chemistry

Track Classification: Fizikālās ķīmijas sēde

Contribution ID: 4

Type: **Oral presentation**

APPROACH OF USING THE OPPOSITE CHIRALITY OF CROWN ETHER STATIONARY PHASES IN CHIRAL RECOGNITION OF TETRAPEPTIDE ENANTIOMERS

Friday, 11 February 2022 13:00 (15 minutes)

Crown ether chiral stationary phases have been successfully used for separating enantiomers of various racemic compounds containing primary amino groups. Although chiral recognition mechanism for crown-ether CSPs is generally understood, on a molecular level, the exact chiral recognition mechanisms for the resolution of short peptides, containing multiple amino moieties capable of binding to the crown ether selector, are still unclear [1].

A research of relationship between the peptide chemical structure and chiral chromatographic interactions was performed, by comparing the retention profiles of μ -opioid receptor agonist tetrapeptide Tyr-Arg-Phe-Lys-NH₂ and eight its structural analogues, synthesized with the aim to selectively exclude interacting amino groups in tetrapeptide sequence on S- and R-(3,3'-diphenyl-1,1'-binaphthyl)-20-crown-6 stationary phases [CR-I (+) and (-)], in order to clarify, which of the potential interaction sites are responsible for chiral recognition in Tyr-Arg-Phe-Lys-NH₂ tetrapeptide. It was established, that, under the same LC conditions, retention of tetrapeptide isomers, fixed in D-tyrosine position on CR-I (+) does not differ significantly from their corresponding LXXX enantiomer on CR-I (-) column and vice versa, demonstrating the capability of roughly estimating the retention times of the corresponding enantiomer.

By assuming, that only in case of stereoselective binding, retention times of single enantiomer on CR-I (+) and (-) columns, under the same chromatographic conditions, would differ from each other, this approach was used to study the retention behaviour of eight tetrapeptide analogues. It was concluded that N-terminal α -amino group in Tyr is responsible for chiral recognition of Tyr-Arg-Phe-Lys-NH₂.

Studies were supported by Latvian Institute of Organic Synthesis internal grants (IG-2020-04; IG-2021-05).

References:

[1] Upmanis T., Kažoka H., Arsenyan P. J. *Chromatogr. A* 2020, 1622, 461152

Primary authors: UPMANIS, Toms; Dr KAŽOKA, Helena (Latvian Institute of Organic Synthesis)

Presenter: UPMANIS, Toms

Session Classification: Physical Chemistry

Track Classification: Fizikālās ķīmijas sēde

Contribution ID: 5

Type: **Oral presentation**

GRAPHENE IN LAYERED NANOSTRUCTURES

Friday, 11 February 2022 16:00 (15 minutes)

Graphene – 2D carbon allotrope – is a unique nanomaterial due to its physical properties: semiconductor with zero band gap, high electrical and thermal conductivity, high optical transparency and mechanical strength. Such properties open wide applications of graphene in many fields such as electronics, optoelectronics, thermoelectrics etc. Combination of graphene with other nanomaterials in layered nanostructures can provide creation of heterostructures with improved physical properties.

In this work the improvement of crystal structure and physical properties of nanomaterials combining them with graphene will be considered on graphene/Bi₂Se₃/graphene layered structures [1], graphene/ZnO nanolaminates [2], graphene/Bi₂Se₃/ZnO heterostructures [3]. The enhancement of properties is predicted from changes in crystal structure during synthesis of nanostructures on graphene substrates (graphene, ZnO and Bi₂Se₃ have similar lattice geometry allowing epitaxial growth onto graphene) and due to charge transfer at the interface of created layered structures. For the fabrication of layered structures chemically vapor deposited graphene was transferred onto supporting quartz substrates and for graphene/ZnO nanolaminates - onto ZnO nanostructures. ZnO nanostructured layers were synthesized using atomic layer deposition technique. Bi₂Se₃ nanostructured coatings were synthesized onto graphene using catalyst-free vapour-solid deposition technique. Morphology and crystal structure of fabricated heterostructures were studied using scanning electron microscopy, atomic force microscopy, X-ray diffractometry. Thermoelectric properties of Bi₂Se₃ in graphene/Bi₂Se₃/graphene layered structures were studied by electrical conductivity and thermoelectric measurements. Optical properties of ZnO in heterostructures were investigated by absorbance and photoluminescence measurements. Correlation between the structure, optical and thermoelectrical properties of semiconductor nanolayers in layered heterostructures is analyzed. Possible mechanisms of improving the optical and thermoelectric properties of graphene-containing layered nanostructures are proposed. Fabricated nanostructures showed the good potential for applications in thermoelectric and optoelectronic devices.

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Primary author: BAITIMIROVA, Margarita

Co-authors: Dr ANDZANE, Jana (Institute of Chemical Physics, University of Latvia); Dr VITER, Roman (Institute of Atomic Physics and Spectroscopy, University of Latvia); Dr BECHELANY, Mikhael (University of Montpellier, European Institute of Membranes, CNRS); Prof. ERTS, Donats (Institute of Chemical Physics, University of Latvia)

Presenter: BAITMIROVA, Margarita

Session Classification: Physical Chemistry

Track Classification: Fizikālās ķīmijas sēde

Contribution ID: 6

Type: **Oral presentation**

Experimental and theoretical study of free volume in silicon-functionalized ionic liquids

Friday, 11 February 2022 11:10 (15 minutes)

Due to the dominating Coulombic interactions, packing of ions in ionic liquids (ILs) solely depends on ion shape and size. The free volume in ILs is thus generally smaller than in molecular liquids. The low volatility and structural tuneability of ILs make them attractive for applications involving gaseous solutes. Greater free volume can entropically contribute to absorption of gases and, for example, allow selective absorption based on size when other solvent-solute interactions are of comparable energy. Understanding of design principles for ILs of higher free volume is therefore crucial towards efficient IL-based materials for gas capture and separation.

In this work we have designed, prepared and characterised new heavily branched ILs containing several silicon atoms within the cation. Dicyanamide $[\text{N}(\text{CN})_2]^-$, tetracyanoborate $[\text{B}(\text{CN})_4]^-$ and bis-(trifluoromethanesulfonyl)imide $[\text{NTf}_2]^-$ were selected as anions due to differences in their size and rigidity. Argon absorption was measured in 9 ILs using a low-pressure isochoric saturation method, and the mole fraction $x(\text{Ar})$ solubilities were used as probe for relative free volumes. In order to validate experimental results and explore argon solvation environment, molecular dynamics simulations were performed utilizing the recently developed CL&Pol polarizable force-field.

Branching in the carbon atom chain leads to significant increase in IL viscosity compared to the linear counterparts, while silicon atom incorporation in their isoelectronic analogues provided a remarkable viscosity reduction. Modelling of cavity size distribution via MD provided a set of argon solubility data that matched the order of experimental solubility measurements. Results of this study demonstrate the usefulness of the methodology of probing and prediction of the free volume in ILs, and shed light on the structural features leading to increased free volume and reduced IL viscosity.

Primary authors: Dr BAKIS, Eduards; Dr GOLOVIZNINA, Kateryna; Dr VAZ, Ines; Prof. PÁDUA, Agilio; Prof. COSTA GOMES, Margarida

Presenter: Dr BAKIS, Eduards

Session Classification: Physical Chemistry and Analytical Chemistry. Joint session

Track Classification: Fizikālās ķīmijas un Analītiskās ķīmijas kopējā sēde

Contribution ID: 7

Type: **Oral presentation**

FINE-TUNING SOLID STATE LUMINESCENCE PROPERTIES OF MOLECULAR CRYSTALS VIA SOLID SOLUTION FORMATION

Friday, 11 February 2022 14:15 (15 minutes)

Solid solutions (SS) are single multicomponent solid phases for which the constituent component ratio can vary in continuum. Along with the composition, also properties of solid solutions are modulated. The changes in composition are often accompanied by a continuous change in some physical and/or chemical properties (e.g., density, solubility, melting point), and more complex properties such as solid-state luminescence and phosphorescence properties, that are composition-dependent.

A.K.A. acknowledges support by 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 “Mikrotikls” doctoral scholarship in the field of natural and medical sciences.

Primary author: Mr SARŠŪNS, Kristaps (University of Latvia, Faculty of Chemistry, Department of Physical Chemistry)

Co-authors: Dr BĒRZIŅŠ, Agris (University of Latvia, Faculty of Chemistry); Dr RĒĶIS, Toms (University of Latvia, Faculty of Chemistry)

Presenter: Mr SARŠŪNS, Kristaps (University of Latvia, Faculty of Chemistry, Department of Physical Chemistry)

Session Classification: Physical Chemistry

Track Classification: Fizikālās ķīmijas sēde

Contribution ID: 8

Type: **Oral presentation**

VITAMIN B12 BLOOD LEVEL VARIATION WITH THE AGE OF PATIENTS

Friday, 11 February 2022 12:10 (15 minutes)

Introduction. It has been shown that determination of reference intervals (RI) using accumulated general patient data can be a cost effective alternative [3] to special research following C28-A3 guidelines[1].

There are some reports on B12 RI for different ethnicities [2]. There is little and somewhat contradictory information about the B12 RI for different age groups and sexes. In this work the method of calculation of B12 reference intervals from large number of general patient data described by Gavars et al. [3] was used to calculate B12 RI intervals for different sexes and age groups.

Materials and methods. Results of 172597 B12 tests accumulated at EGL from 1st of January 2018 till 21st of November 2021 were used. B12 values were obtained using standard clinical laboratory technique and procedure. Data set consisted of 150 to 400 test results for each one year age interval at the age of 1 to 10 years, and more than 1000 test results for each one year age interval at the ages over 21 years. Mean B12 value and RI was calculated for each age group by 2 years steps. RI interval was calculated by fitting patient density distribution to Gaussian distribution and using only one third of patient data – only those patient data that were close to the mean B12 value were used in the fitting procedure.

Results. High quality B12 mean value and RI data were obtained for each age group and both sexes. Results show distinct variation of B12 mean value with the age of patients. For children B12 mean value raises from 449 pg/l at the age of 1 year to maximum of 665 pg/l at 5-7 years of age. Then the B12 mean value declines to minimum of 410 pg/l at the age of 20 years. From age 23 to 35 the mean B12 value gradually increases to 470 pg/l and stays almost constant during the rest of the lifespan. The calculated reference interval follows the same trend. The difference between calculated high and low RI starts to increase at older age, starting at approximately 60 years of age.

Conclusion. A systematic variation of B12 blood level values with the age was observed with B12 blood level peaking at the age of 5-7 years. Lowest B12 blood level was observed at the age of 17-23 years.

References:

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- [3] D. Gavars et al. submitted to Proceedings of the Latvian Academy of Sciences. Section B: Natural, Exact, and Applied Sciences

Primary author: Mr GAVARS, Didzis (Egils Gulbis Laboratory, Riga Stradiņš University)

Co-authors: Dr AUCE, Agris (Institute of Chemical Physics, University of Latvia); Mr TAUCKELS, Eriks (Egils Gulbis Laboratory); Mrs LINDENBERGA, Ilze (Egils Gulbis Laboratory); Mr PERMINOVs, Dmitrijs (Egils Gulbis Laboratory, Institute of Chemical Physics, University of Latvia); Mrs TUTANE, Anna Inese (Egils Gulbis Laboratory, Riga Stradins University); Ms MIKELSONE, Agnese (Riga Stradins University)

Presenters: Dr AUCE, Agris (Institute of Chemical Physics, University of Latvia); Ms MIKELSONE, Agnese (Riga Stradins University)

Session Classification: Physical Chemistry and Analytical Chemistry. Joint session

Track Classification: Fizikālās ķīmijas un Analītiskās ķīmijas kopējā sēde

Contribution ID: 9

Type: **Oral presentation**

CYCLODEXTRIN BASED METAL ORGANIC FRAMEWORK CRYSTALLIZATION AND EVALUATION AS POTENTIAL DRUG CARRIER

Friday, 11 February 2022 13:45 (15 minutes)

Metal–organic frameworks (MOFs) have been known for decades, and they continuously have gained interest because of their application potential increasing in the various fields – pharmacy, medicine, technology etc [1]. MOFs porous architecture and adjustable properties 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].

In this study different cyclodextrin based MOFs were crystallized using various methods and characterized by X-ray methods. At the results we obtained new crystal structures for α -CD-K MOF in crystallization using vapor diffusion method. New crystal structure for β -CD-K MOF using solvent exchange method. New crystal phase for γ -CD-K using fast crystallization. All crystal forms were compared and evaluated as potential drug carriers.

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”.

References:

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Primary authors: MISHNEV, Anatolijs (Latvian Institute of Organic Synthesis,); KRŪKLE-BĒRZIŅA, Kristīne (Latvian Institute of Organic Synthesis); ŠUBINS, Kirills (Latvian Institute of Organic Synthesis)

Presenter: KRŪKLE-BĒRZIŅA, Kristīne (Latvian Institute of Organic Synthesis)

Session Classification: Physical Chemistry

Track Classification: Fizikālās ķīmijas sēde

Contribution ID: 10

Type: **Oral presentation**

MIRCOCALORIMETER PERFORMANCE DETERMINATION AND STABILITY DETERMINATION OF NITROCELLULOSE-BASED SUBSTANCES AND THEIR COMPARISON WITH CHROMATOGRAPHIC RESULTS

Friday, 11 February 2022 15:15 (15 minutes)

Nitrocellulose-based substances are dangerous because of their instability; therefore, stabilizers are added, but due constant chemical reactions, they are depleted, that's why for safety of everyone involved, nitrocellulose-based substance stability must be tested. In the last few years Latvia started to test its own munition on chemical stability, which was limited to chromatographic methods, but now an opportunity arose to test it with microcalorimetry and in addition compare the obtained results between two methods.

Microcalorimeter performance was determined via two methods, one being internal test and the second one being biphenyl test. Internal test results were in agreement with instrument requirements, whereas biphenyl test showed slight deviation from requirements for one of six microcalorimeters at 1,8 %.

Analysed munition samples, delivered by Latvian National Armed Forces, contained two different stabilisers. First stabiliser was diphenylamine, samples with this stabiliser showed that it would be stable for up to ten years at 25 °C, but one of the samples was nearing its limits. Another stabiliser was centralite I or ethylcentralite. Samples containing centralite I displayed almost no deviation from the baseline, therefore it can be stored and safely used.

The obtained results with chromatographic methods displayed similar results, samples containing diphenylamine displayed slight decrease in stabiliser content after aging, where in one of the samples the decrease was quite extensive. Samples with centralite I displayed almost no decrease in stabiliser content after aging, which was around 0,1%.

Primary author: MEIJERS, Kaspars

Co-author: Dr MEKŠS, Pēteris

Presenter: MEIJERS, Kaspars

Session Classification: Physical Chemistry

Track Classification: Fizikālās ķīmijas sēde

Contribution ID: 11

Type: **Oral presentation**

Exploring aspartic protease inhibitor binding to design selective antimalarials

Friday, 11 February 2022 11:40 (15 minutes)

Selectivity is a major issue in the development of drugs targeting pathogen aspartic proteases. Here we explore the selectivity determining factors by studying specifically designed malaria aspartic protease (plasmepsin) open-flap inhibitors. 2-Aminoquinazolin-4(3H)-one based plasmepsin inhibitors with various flap pocket substituents are synthesized and their potencies against several aspartic proteases are determined. Metadynamics simulations are used to uncover the complex binding/unbinding pathways of these inhibitors, and describe the critical transition states in atomistic resolution. Our findings demonstrate that plasmepsin inhibitor selectivity can be achieved by targeting the flap loop with hydrophobic substituents that enable ligand binding under the flap loop, as such behaviour is not observed for several other aspartic proteases. The ability to estimate compound selectivity before they are synthesized is of great importance in drug design, therefore, we expect that our approach will be useful in selective inhibitor design not only against aspartic proteases, but other enzyme classes as well.

Primary authors: Prof. JIRGENSONS, Aigars; Dr RASINA, Dace; Ms ZELENKOVA-GOPEJENKO, Diana; Mr BASENS, Emils Edgars; BOBROVS, Raitis; Mr LEITIS, Gundars; Mrs KANEPE, Iveta; Mr VELINS, Karlis Kristofers; Prof. JAUDZEMS, Kristaps; Mrs DRUNKA, Laura; Mrs MATISON, Sofija; Dr ANDRIANOV, Victor

Presenter: BOBROVS, Raitis

Session Classification: Physical Chemistry and Analytical Chemistry. Joint session

Track Classification: Fizikālās ķīmijas un Analītiskās ķīmijas kopējā sēde

Contribution ID: 12

Type: **Oral presentation**

COST GAINS AND CO2 REDUCTION IN GREENHOUSE HEATING BY AIR TO WATER HEATPUMP LATVIA DURING 2ND HALF OF 2021.

Friday, 11 February 2022 15:30 (15 minutes)

Use of air to water heatpump (AWHP) to reduce CO₂ emissions from greenhouse heating were investigated by calculating the running costs of AWHP and natural gas boilers. Real climatic conditions and heating regimes of SIA Rītausma industrial greenhouse production facility in south east of Latvia were used for the calculations. COP of commercially available Hitachi 10kw heating power air-to water heatpump and the Nordpool day-ahead Latvia electricity prices were used. AWHP COP was adjusted to the actual outdoor temperature by using the third-degree polynomial fitted to the COP declared by the producers at 4 standard temperatures: -7,2,7,12 C. The cost of gas heating was calculated from the actual price of natural gas delivered to the facility and the actual gas boiler which has a 0,94 COP.

Results. 2nd half of 2021 was extraordinary in terms of hikes in both electricity and natural gas prices. For most of the time AWHP economically outperformed gas heating by a large margin. During periods of very high electricity prices and low temperatures the gas was much better option economically. During the time period studied the AWHP had economic advantages from August to November 2021 and gas heating was better during most of December 2021. By adding heatpumps to the existing gas heating system and running a hybrid system it proved possible to lower heating costs at least twice as compared to the existing cost of heating by natural gas alone. Addition of heatpumps to existing gas heating allows for at least 2-to-3-fold reduction of CO₂ emissions and a significant reduction of the heating costs. Phase transition materials like paraffins with phase transition T 50-60 C were found to be the most efficient storage media for the heat generated by AWHP in order to benefit from low electricity night prices at Nordpool.

Summary. Calculations using theoretical performance of heatpumps and market price for electricity and gas in Latvia during 2nd half of 2021 show that it is possible to achieve 2-to-3-fold reduction in CO₂ emissions and simultaneously significantly decrease the heating costs by adding air to water heatpump to existing gas heating for a greenhouse in Latvia.

Project "Research of effective heat production and supply solutions in covered areas" is supported by the Ministry of Agriculture and the Rural Support service in the programme 16.1 "support for the establishment and operation of operational groups of the EIP for agricultural productivity and sustainability". Nr.18-00-A01612-000023

Primary authors: AUCE, Agris; JEREMUSS, Aivars; Mr HORNS, Indulis Andris; AUCE, Ivars; DROZDOVS, Mareks; GRĪNBERGS, Uģis; RUCIŅŠ, Ādolfs

Presenter: AUCE, Agris

Session Classification: Physical Chemistry

Track Classification: Fizikālās ķīmijas sēde

Contribution ID: 13

Type: **Oral presentation**

Metallic nanoparticle dispersions for conducting ink preparation

Friday, 11 February 2022 16:45 (15 minutes)

Metallic nanoparticle dispersions for conducting ink preparation

Aleksandrs Novikovs, Boriss Poļakovs
Institute of Solid State Physics, University of Latvia
e-mail: aleksandrs.novikovs@cfi.lu.lv

The aim of this research is to prepare conducting nanoparticle inks, such that it would be possible to print electrical components using a functional ink-jet printer.

Relevance of the topic is related to preparation of cheap and wearable electrical circuits, preparation of RFID antennas, preparation of sensors.

Following nanoparticles for inks were prepared: silver spherical nanoparticles in water, silver triangle nanoprisms in water, copper spherical nanoparticles in hexane, copper spherical nanoparticles with silver shell in hexane and nickel spherical nanoparticles in hexane. Prepared dispersions were characterized with SEM or TEM microscopy, UV-Vis spectroscopic methods, XRD, DLS, electrical conductivity was estimated and aggregation stability. In all dispersions nanoparticle size is less than 100 nm. All samples were sintered at 150o, 200o, 250o, 300o C temperatures and after that those samples were analyzed with SEM. It can be concluded, that it is possible to formulate inks using these particles, and it may be possible to use these to print electrical components.

The financial support of ERAF project Nr. 1.1.1.1/20/A/060 is greatly acknowledged.

Primary authors: NOVIKOVs, Aleksandrs (LU CFI, LU FAM DSP); POĻAKOVs, Boriss

Presenter: NOVIKOVs, Aleksandrs (LU CFI, LU FAM DSP)

Session Classification: Physical Chemistry

Track Classification: Fizikālās ķīmijas sēde

Contribution ID: 14

Type: **Oral presentation**

Mass-separation of $^{43,44,47}\text{Sc}$ radionuclides from irradiated natural Ti targets at the CERN-MEDICIS facility

Friday, 11 February 2022 16:15 (15 minutes)

Medical radionuclides as $^{43,44m,44g,47}\text{Sc}$ are very promising in “matched theranostic pair” radio-pharmaceutical development for cancer treatment. Use of natural titanium as target material for production of $^{43,44m,44g,47}\text{Sc}$ radionuclides is favorable in terms of cost and the wide availability of target material, in contrast of using low abundant enriched Ca targets. We report here the recent studies, development, production and extraction of scandium radionuclides from irradiated thick natural titanium targets at MEDICIS at CERN.

In this work, natural titanium targets were irradiated at the MEDICIS target irradiation station with 1.4 GeV protons delivered by the CERN Proton Synchrotron Booster (PSB). Although nuclear reaction cross-sections of $^{43,44m,44g,47}\text{Sc}$ for nat-Ti(p,x) confirm that enough production yield can be achieved to synthesize radio-bioconjugates for imaging studies [1], the presence of contaminant isotopes such as long lived Sc-46 in radiopharmaceutical precursor is not acceptable. To overcome this obstacle, Sc radionuclide purification step, according to their mass using the Isotope Separator OnLine (ISOL) technique and the MEDICIS mass-separator was introduced. The separation of Sc and Ti as elemental radioactive beams is challenging due to their reactive nature, high boiling points and low vapour pressure. Therefore, formation of more volatile molecules, extraction and collection of desired radionuclides were introduced.

Low intensity radioactive Sc^+ and ScF^+ beams with W surface ion source have been reported at ISOLDE [2]. In this work, ScF_x^+ ($x=1-2$) and natTiF_y^+ ($x=1-3$) molecular beams in natural Ti target material and natural Ta target structure ambience have been obtained with a Versatile Arc Discharge Ion Source (VADIS). Also, optimal radionuclide extraction and separator operation parameters were yet to be determined.

We hereby report our results on the positive effect of volatile rare earth and refractory metal molecular beam formation for isotopically pure $^{44,47}\text{Sc}$ extraction and mass-separation. Although ISOL and mass-separation is mandatory, chemical separation step on the collected elements must be done to separate from presence of isobars in the collection foil.

Primary authors: MAMIS, Edgars (Institute of Chemical Physics, University of Latvia, CERN); Prof. PAJUSTE, Elina (Institute of Chemical Physics, University of Latvia); STORA, Thierry (CERN); ROTHE, Sebastian (CERN); CHEVALLAY, Eric (CERN); DUCHEMIN, Charlotte (CERN); RADZIŅA, Maija (Faculty of Medicine, University of Latvia,)

Presenter: MAMIS, Edgars (Institute of Chemical Physics, University of Latvia, CERN)

Session Classification: Physical Chemistry

Track Classification: Fizikālās ķīmijas sēde

Contribution ID: 15

Type: **Oral presentation**

MECHANOCHEMICAL PREPARATION OF CRYSTAL FORMS OF SELECTED PHARMACEUTICAL SUBSTANCES

Friday, 11 February 2022 14:30 (15 minutes)

The most common method used to control polymorphism is crystallization. An alternative to the most commonly used solvent crystallization is a mechanochemical treatment of a crystalline substance or a mixture of more than one substance. Mechanochemistry is defined as chemical synthesis induced by external mechanical energy, such as grinding two solids using a mortar-and-pestle, ball-mill, or shaker. Such reactions are classified as Green Chemistry synthesis, prioritizing high yields, mild conditions and low to no use of solvents.

To date, three polymorphic forms of 3-hydroxybenzoic acid have been described. Similarly, crystal structures of three polymorphs have been found for co-crystal formed between urea and barbituric acid.

Primary author: ČERPAKOVSKA, Zane

Co-authors: BĒRZIŅŠ, Agris; KONS, Artis (University of Latvia)

Presenter: ČERPAKOVSKA, Zane

Session Classification: Physical Chemistry

Track Classification: Fizikālās ķīmijas sēde

Contribution ID: 16

Type: **Oral presentation**

Impact of physical pretreatment on thermal properties of coursed sheep wool fibers

Friday, 11 February 2022 15:45 (15 minutes)

Sheep breeding in Latvia in the last decade is stabilized and continues to develop. Since sheep breeding includes producing of wool, it is important for fabrication of textiles and thermoinsulators. However, annually tons of wool fibers, that do not fit to requirements to be used in textile industry, remain as residues. Such wool can be used as sorbent [1] or convert in activated carbon [2] and use in air filters. In order to increase the area of applications, various treatment methods can be applied, such as chemical [3] or radiation modification [4].

In the present research impact of physical treatment is investigated. Coursed sheep wool was felted (Ltd. Sunakstes Vilnas nams). Non-felted and felted wool was held under various conditions: exposure to light, decreased temperature, moisture, etc. Non-exposed and exposed wool fibers analyzed using thermogravimetry/differential thermal analysis (TG/DTA) method combined with Fourier transform infrared (FTIR) spectrometry. Analysis performed up to 1000°C. Volatile compounds, that are released during heating process, are analysed by registering FTIR spectra with Bruker Vertex 70v equipped with a gas cell and liquid nitrogen – HgCdTe detector.

The obtained results show that coursed sheep wool has three main mass decrease steps, first related with water vapor release, in FTIR spectra are characteristic peaks in ranges of 1500-1700cm⁻¹ and 3000-3700cm⁻¹. Second step is followed by occurring of number of peaks in the FTIR spectra such as at 2850 and 2920cm⁻¹ related to -CH₂ and -CH₃ groups, CO [5] with maximal intensities around 2180 and 2120cm⁻¹, CO₂ centered around 675, 2345 and 3580-3740cm⁻¹ and others. Third main mass loss is followed by release of CO₂. TG data show that up to 400°C the decomposition pattern is similar for both felted and non-felted wool. The obtained results will be used for developing recommendations for producing activated carbon from biofibers.

Research is performed within the frames of ERDF 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”

Primary author: Mr NESENBURG, Janis (Riga Technical University)

Co-authors: AVOTINA, Liga (University of Latvia, Institute of Chemical Physics); Dr ZARINS, Arturs (University of Latvia, Institute of Chemical Physics); Ms GRICENKO, Taisija (University of Latvia, Institute of Chemical Physics); Mr HALITOV, Mihails (University of Latvia, Institute of Chemical Physics); Dr KIZANE, Gunta (University of Latvia, Institute of Chemical Physics)

Presenter: AVOTINA, Liga (University of Latvia, Institute of Chemical Physics)

Session Classification: Physical Chemistry

Track Classification: Fizikālās ķīmijas sēde

Contribution ID: 17

Type: **Oral presentation**

X-RAY INDUCED DEFECTS IN LITHIUM ORTHOSILICATE AND LITHIUM METATITANATE CERAMICS PREPARED USING SOLID STATE SYNTHESIS METHOD

Friday, 11 February 2022 16:30 (15 minutes)

Lithium orthosilicate (Li_4SiO_4) and lithium metatitanate (Li_2TiO_3) for radiation-induced defect studies have been made using numerous methods including sol-gel, melt-spraying, drip-casting and solid-state reaction process in order to evaluate radiation stability of material for application as tritium breeding ceramics in future thermonuclear fusion reactors [1,2]. Solid-state reaction process has many advantages, such as high yield and easy scalability [3], however, to confirm the radiation stability of the material synthesized using this method, the formation and accumulation of radiation-induced defect must be assessed.

In this study, Li_4SiO_4 , Li_4SiO_4 with additions of Li_2TiO_3 , Li_2TiO_3 powder samples obtained by solid-state synthesis route as well as mechanically mixed Li_4SiO_4 and Li_2TiO_3 powders were pressed into 10 mm pellets using manual hydraulic press at room temperature in air. Afterwards, the prepared pellets were irradiated with X-rays in high vacuum with pressure less than 10^{-2} Pa at room temperature using an X-ray tube with wolfram anode. Operating parameters are as follows: 40 kV, 10 mA, irradiation time 15 minutes, and pressed pellet distance from X-ray tube is approx. 15 cm. The total concentration of formed and accumulated X-ray induced defects was assessed using electron paramagnetic resonance (EPR) spectrometry and thermally stimulated luminescence (TSL) technique.

The obtained results show that Li_2TiO_3 had the lowest concentration of both EPR and TSL active X-ray induced defects. The concentration of TSL active defects in the Li_4SiO_4 pellets with additions of Li_2TiO_3 significantly exceeded those detected in Li_2TiO_3 , Li_4SiO_4 pellets and in mechanically mixed Li_4SiO_4 and Li_2TiO_3 samples.

This study has been performed within the framework of the European Regional Development Fund (ERDF) project (application No. 1.1.1.2/VIAA/4/20/614).

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Primary author: TOMELE, Madara (University of Latvia, Institute of Chemical Physics)

Co-authors: SEŅKO, Mareks; ZARIŅŠ, Artūrs; ZOLOTARJOVS, Aleksejs; BAUMANE, Larisa; ĶIZĀNE, Gunta

Presenter: TOMELE, Madara (University of Latvia, Institute of Chemical Physics)

Session Classification: Physical Chemistry

Track Classification: Fizikālās ķīmijas sēde

Contribution ID: 18

Type: **Oral presentation**

PLASMEPSIN II LABELING STRATEGIES TO STUDY CONFORMATIONAL CHANGES OF BINDING SITE WITH NMR SPECTROSCOPY

Friday, 11 February 2022 13:30 (15 minutes)

Malaria infection in humans is caused by *Plasmodium Falciparum* parasite. *P. Falciparum* aspartic proteases (plasmepsins) are responsible for catalytic hemoglobin degradation and thus are being investigated as potential drug targets. Plasmepsins, however, share high structural similarity with human aspartic proteases, emphasizing the need for selective inhibitors. Selectivity of several known plasmepsin inhibitors is attributed to unusual binding under the flap loop [1]. One of the methods that can be used to characterize binding site dynamics upon inhibitor binding is NMR spectroscopy, however, due to large plasmepsin II size, selective protein labeling is required. Here we present two selective protein labeling strategies.

Substitution of certain amino acids with their fluorinated analogues can be exploited to study conformational changes with ^{19}F NMR spectroscopy. In this study tryptophan was chosen as amino acid of interest due to its position near the binding site and low number of residues. Labeled protein was obtained using biosynthetic amino acid incorporation [2].

Second method used was spin labeling with a molecule containing nitroxide moiety. Paramagnetic groups such as MTSL (*S*-(1-oxyl-2,2,5,5-tetramethyl-2,5-dihydro-1H-pyrrol-3-yl)methyl methane-sulfonothioate) increase relaxation rate of nearby atoms, allowing to estimate inter-atomic distances up to 25 Å, and, thus, exact position of inhibitor in the binding site. MTSL label was attached to cysteine residue that was introduced in the flap loop using site-directed mutagenesis [3]. Obtained NMR spectra show that both labels have been successfully incorporated in plasmepsin II molecule, however, protein preparation, yields and recording conditions of NMR spectra still need to be optimized in order to apply these methods to protein dynamics studies.

Primary author: DRUNKA, Laura (Latvian Institute of Organic Synthesis)

Co-author: BOBROVS, Raitis

Presenter: DRUNKA, Laura (Latvian Institute of Organic Synthesis)

Session Classification: Physical Chemistry

Track Classification: Fizikālās ķīmijas sēde

Contribution ID: 19

Type: **Oral presentation**

IDENTIFICATION OF THE MAIN DYESTUFFS PRESENT IN BARKS OF ALDERS, BIRCH, OAK AND ASPEN

Friday, 11 February 2022 13:15 (15 minutes)

Substantial amounts of bark of forest trees are a by-product of wood processing, a major proportion of which is used for energy production. Nevertheless, it could also be a valuable source of tannins for use as natural colourants [1]. The barks of many trees are suitable sources of reddish-brown dyes. The most frequently mentioned brown-colouring barks were tannin-rich alder, oak, hemlock and maple [2]. Hydroxyl groups of tannins have capability form effective bonds with protein fibres and dyes to provide fix dyes by nonspecific bonding. Commonly, plant tannins (catechins, proanthocyanidins and polyphenols) have a strong affinity for proteins. Tannins together with metallic salt mordants form metal tannates, resulting in better colour fastness [2,3].

The popular dye trees of Latvia summarized in the listing of plant dyes are: black alder (*Alnus glutinosa*), grey alder (*Alnus incana*), silver birch (*Betula pendula*), juniper (*Juniperus communis*), alder buckthorn (*Frangula alnus*), pedunculate oak (*Quercus robur*), bird cherry (*Padus avium*), aspen (*Populus tremula*), European crab apple (*Malus sylvestris*), ash (*Fraxinus excelsior*) [4, 5]. Dyeing process and materials used in farmsteads differed from the ones practiced by professional dyers. The peasants were employed birch bark in dyeing, mainly in light browns, blacks or other drab colours. The professional dyers obtained brighter tones and fastness of colours. Oaks were used by 18th- and 19th-century professional dyers, for they contained tannins and other dyeing agents which would give woollens stable colours [2].

The objective of the present study was to evaluate the extracts of black alder, grey alder, pedunculate oak, silver birch and aspen as natural textile dye. The dyeing solutions of barks were analysed by UPLC-DAD-MS. The preliminary results show that barks are a valuable source of tannins for use as natural colourants. Hydrolysable tannins (gallic acid, ellagic acid) and condensed tannins (catechin, procyanidins) were found in water extracts from tree barks.

Primary author: VALKOVSKA, Valda

Co-author: OROLA, Liāna

Presenter: VALKOVSKA, Valda

Session Classification: Physical Chemistry

Track Classification: Fizikālās ķīmijas sēde

Contribution ID: 20

Type: **Oral presentation**

THERMAL ANALYSIS AND IR SPECTROSCOPY USAGE TO DETERMINE THE DEGREE OF SULFONATION OF SPEEK

Friday, 11 February 2022 17:00 (15 minutes)

As the use of ion exchange membranes increases, so does the need to improve them. SPEEK membranes are described using their sulfonation degree (DS) that is directly related to other membrane parameters. The degree of sulfonation is defined as the percentage of re-sulfonated SPEEK units. Therefore, it is necessary to find a cheap, easy-to-perform and accurate method for testing DS. The examination of sulfonated polyether ether ketone membranes and ionic liquids was performed using thermogravimetry and Fourier transform infrared spectroscopy methods at the Institute of Solid Phase Physics. Previously formed membranes and ionic solutions were heated in the thermogravimeter LABSYS Evo. The evaporated portion released during the experiment was transferred to an infrared spectrophotometer for analysis using argon as a carrier gas.

Primary authors: BOGDANOVŠ, Dmitrijs; VAIVARS, Guntars; SPRŪĢIS, Einārs

Presenter: BOGDANOVŠ, Dmitrijs

Session Classification: Physical Chemistry

Track Classification: Fizikālās ķīmijas sēde

Contribution ID: 21

Type: **Oral presentation**

USE OF SELECTIVE MOF FORMATION FOR SEPARATION OF α -, β - AND γ -CYCLODEXTRINS

Friday, 11 February 2022 14:45 (15 minutes)

Cyclodextrins (CD's) are cyclic oligosaccharides widely used in pharmaceutical, food and cosmetic industries as excipients and stabilizers. They are produced by enzymatic transformation of starch, obtained from renewable green sources (potato, corn, etc.). This process is unselective and typically leads to a formation of a mixture of CD's with various numbers of glucose subunits in the cycle (6 for α , 7 for β and 8 for γ). One of approaches to their separation is a selective formation of a metal-organic framework (MOF), where a CD molecule serves as a ligand [1].

In order to create an efficient, sustainable and scalable separation process behavior of various CD mixtures was investigated under MOF crystallization conditions. In all cases crystallization of MOF was carried out in the presence of Na_2CO_3 in aq. MeOH. The precipitated material was investigated by powder X-ray diffractometry and obtained results are summarized on ternary diagram (Figure 1).

Fig. 1. Ternary diagram of crystalline products obtained from various compositions of β -CD, γ -CD and Na_2CO_3 with different mass ratios (border lines between phases are put for clarity, they are not accurate).

α -CD remained in solution in a wide range of concentrations (10-90 mass% from the total mass of CD's). It was excluded and a variable amount of Na_2CO_3 was included in the diagram instead. The least soluble β -CD dominates in the solid phase when its amount in solution is >50 mass%; while in the 20-50 mass% range a mixture β -CD + γ -CD-Na MOF is precipitated. Low concentrations of Na_2CO_3 (<10 mass%) lead to precipitation of γ -CD-MeOH solvate with a low yield. At a higher concentration of Na_2CO_3 (>40 mass%) γ -CD-Na is formed, but it is contaminated with Na_2CO_3 . The most efficient crystallization of pure γ -CD-Na was achieved in 10-40 mass% range of Na_2CO_3 with <20 mass% of β -CD.

This research was supported by a project "Development of innovative face cosmetics with controlled release of active ingredients by use of Metal Organic Frameworks or Cocrystals" (ERAF project number 1.1.1.1/18/A/176).

References:

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Primary authors: ŠUBINS, Kirills (Latvian Institute of Organic Synthesis); KRŪKLE-BĒRZIŅA, Kristīne (Latvian Institute of Organic Synthesis); BEĻAKOVŠ, Sergejs (Latvian Institute of Organic Synthesis)

Presenter: KRŪKLE-BĒRZIŅA, Kristīne (Latvian Institute of Organic Synthesis)

Session Classification: Physical Chemistry

Track Classification: Fizikālās ķīmijas sēde

Contribution ID: 22

Type: **not specified**

Opening

Friday, 11 February 2022 10:30 (10 minutes)

Presenter: BERZINS, Agris

Session Classification: Physical Chemistry and Analytical Chemistry. Joint session

Contribution ID: 23

Type: **not specified**

Application of Wastewater – Based Epidemiology for Tracking Human Exposure to Deoxynivalenol and Enniatins

Friday, 11 February 2022 10:55 (15 minutes)

Presenter: BERZINA, Zane

Session Classification: Physical Chemistry and Analytical Chemistry. Joint session

Contribution ID: 24

Type: **not specified**

Bioactivity Enhancement of Peo Coatings by Introduction of Amorphous Calcium Phosphate Particles

Friday, 11 February 2022 11:25 (15 minutes)

Presenter: GREBŅEVS, Vladlens (Faculty of Chemistry, Department of Analytical Chemistry)

Session Classification: Physical Chemistry and Analytical Chemistry. Joint session

Contribution ID: 25

Type: **not specified**

Qualitative Fingerprinting of Psychoactive Pharmaceuticals, Illicit Drugs, and Related Human Metabolites in Wastewater During the Covid-19 Pandemic in Riga, Latvia

Friday, 11 February 2022 11:55 (15 minutes)

Presenter: PERKONS, Ingus

Session Classification: Physical Chemistry and Analytical Chemistry. Joint session