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# Chemistry & Chemical Technology

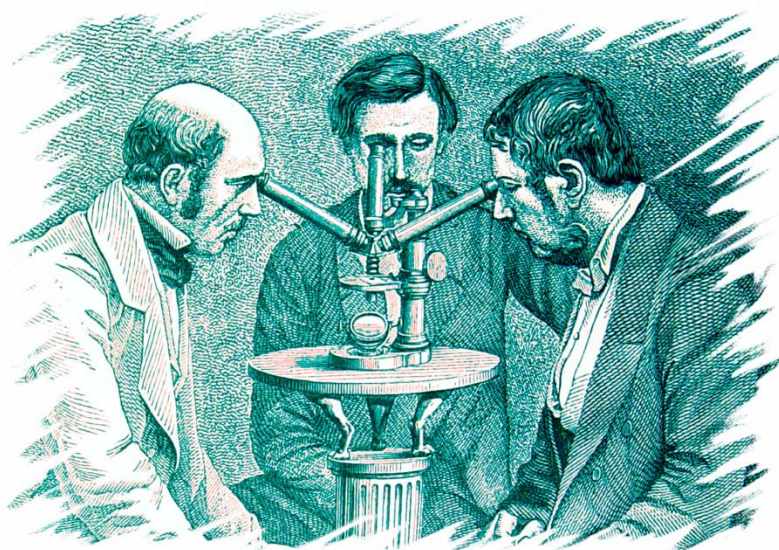


Vilnius University Press



CTT-2019

# CONFERENCE BOOK



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**2019 May 16 | 8 AM to 16 PM |  
LITHUANIAN ACADEMY OF SCIENCES  
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THE AIM OF THE CONFERENCE IS TO BRING TOGETHER YOUNG SCIENTISTS, ENGINEERS, RESEARCHERS AND STUDENTS OF LITHUANIAN UNIVERSITIES, INSTITUTES, CENTERS OF SCIENCE AND BUSINESS TO CARRY OUT RESEARCH IN THE FIELD OF CHEMISTRY AND CHEMICAL TECHNOLOGY, TO PROVIDE THE OPPORTUNITY TO EXPAND KNOWLEDGE AND PRESENT THE LATEST SCIENTIFIC RESULTS AND IDEAS.

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ISBN/ISMN 978-609-07-0167-6

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# Organizing and scientific committees, sponsors

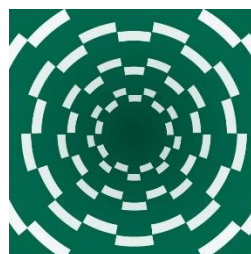
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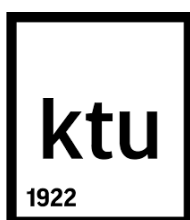
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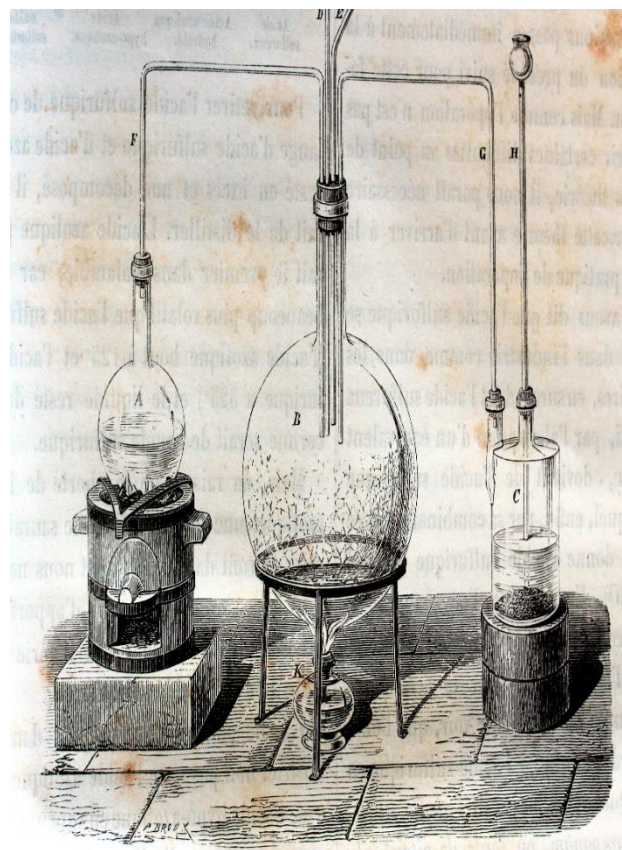
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**CENTER**  
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# Conference Program

**16<sup>th</sup> May**

**Venue:** Lithuanian Academy of Sciences, Gedimino av. 3, Vilnius

Time	Presenter	Institution	Title of the Lecture
8:00 – 9:00	<b>Registration of participants</b>		
9:00 – 9:10	<b>Welcome speech of Vilnius University Rector Prof. A. Zukauskas</b>		
9:10 – 9:15	<b>Welcome speech of Vilnius University Faculty of Chemistry and Geosciences Dean Prof. A. Beganskiene</b>		
9:15 – 9:45	Invited Speaker prof. dr. Fabio Marchetti	University of Camerino, Italy	Novel composite materials for antimicrobial applications
9:45 – 10:15	Invited Speaker prof. dr. Zineb Mekhalif	Namur University, Belgium	Electrochemistry and Surface Chemistry: a powerful combination for nanotechnology
10:15 – 10:45	Invited Speaker prof. dr. Ismail Hakki Boyaci	Hacettepe University, Ankara, Turkey	Raman and SERS-based detection of Gene and Microorganisms
10:45 – 11:45	<b>Poster session I and coffee break</b>		
11:45 – 12:15	Invited Speaker dr. Magdalena Oćwieja	Polish Academy of Sciences, Krakow, Poland	Noble metal nanoparticle layers of tunable coverage, structure and charge
12:15 – 12:45	Invited Speaker prof. dr. Sheng-Tung Huang	National Taipei University of Technology, Taiwan	Design strategies and applications of self-immolative chemical probes for biosensing
12:45 – 13:45	<b>Lunch Break (free time)</b>		
13:45 – 14:00	Tadas Matijošius	Center for Physical Sciences and Technology, Lithuania	Penetration of titanium into alumina nanopores after atomic layer deposition or magnetron sputtering
14:00 – 14:15	Prof. dr. Aušra Valiūnienė	Vilnius University, Lithuania	Fast Fourier transform electrochemical impedance spectroscopy for monitoring surface modification
14:15 – 14:30	Aušra Adomėnienė	Kaunas University of Technology, Lithuania	Enzyme inhibitory activity of hydroethanolic extract of yam ( <i>dioscorea caucasica</i> lipsky) leaves

14:30 – 15:00	<b>Coffee break</b>		
15:00 – 15:15	Lijana Dienaitė	Kaunas University of Technology, Lithuania	Antioxidant capacity and phytochemical composition of guelder-rose berry pomace extracts
15:15 – 15:30	Prof. dr. Artūras Katelnikovas	Vilnius University, Lithuania	Rare Earth Elements: Industrial Applications
15:30 – 15:45	Dobrochna Rabie	Nicolaus Copernicus University in Toruń, Poland	Determination of storage conditions of refined rapeseed oil fortified with phenolic acid esters
15:45 – 16:00	Dr. Alanas Petrauskas	Aukštieji algoritmai	It's not what we know – it's how we think!
16:00 – 17:00	<b>Poster session II</b>		
17:00 – 17:15	<b>The Best Posters Awards and Conference Closing Ceremony</b>		
18:00 – 20:00	<b>Conference Gala dinner</b>		

## POSTER SESSION I 10:45 – 11:45

### Inorganic chemistry

<b>P01</b>	<u>R. Aukštakojytė</u> , J. Gaidukevič, J. Barkauskas	MALONIC ACID ASSISTED REDUCTION OF GRAPHITE OXIDE: STRUCTURAL CHARACTERISATION
<b>P02</b>	<u>K. Baltakys</u> , G. Sarapajevaite, V. Rudelis	WAYS OF SULFUR WASTE RE-USE UNDER HYDROTHERMAL CONDITIONS
<b>P03</b>	<u>M. Baublytė</u> , M. Liubinienė, A. Beganskiene	HYDROGEL AND ENZYMES COMBINATION FOR PAPER DOCUMENTS CLEANING
<b>P04</b>	<u>A. Bronušienė</u> , I. Ancutienė	XRD STUDY OF THIN SnS FILMS ON FTO GLASS
<b>P05</b>	<u>I. Grigoraviciute-Puroniene</u> , V. Vegelyte, A. Kareiva	SYNTHESIS OF LOW CRYSTALLINE CALCIUM DEFICIENT HYDROXYAPATITE GRANULES
<b>P06</b>	<u>G. Inkrataitė</u> , A. Popov, R. Skaudžius	PREPARATION AND CHARACTERIZATION OF LUAG AND YAG BASED SCINTILLATION MATERIALS
<b>P07</b>	<u>M. M. Kaba</u> , A. Smalenskaite, I. Morkan, A. Kareiva	ON THE WET CHEMISTRY PREPARATION OF LAYERED DOUBLE HYDROXIDE AND MIXES-METAL OXIDE COATINGS
<b>P08</b>	<u>D. Karoblis</u> , A. Zarkov, A. Kareiva	SYNTHESIS OF (1-x)BaTiO <sub>3</sub> ·xBiMnO <sub>3</sub> SOLID SOLUTIONS VIA SOL-GEL METHOD
<b>P09</b>	<u>N. Kybartienė</u> , G. Urbonavičiūtė	INFLUENCE OF CALCINED CLAY ON THE EARLY HYDRATION OF ANHYDRITE BINDING MATERIAL
<b>P10</b>	<u>I. Knabikaitė</u> , K. Baltakys, T. Dambrauskas, A. Eisinis	THE INFLUENCE OF COBALT IONS ON COMPOUNDS FORMATION PROCESS IN CaO-SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -H <sub>2</sub> O SYSTEM

<b>P11</b>	<u>A.Kunciute</u> , R.Ivanauskas, A.Ivanauskas	COPPER-DOPED TIN(II) SELENIDE THIN FILMS
<b>P12</b>	I. Lebedyte, <u>I.Mikalauskaite</u> , G. Plečkaiyte, A. Beganskiene, A. Kareiva	UPCONVERSION LANTHANIDE-DOPED NaYF <sub>4</sub> NANOCRYSTALS COATED WITH SILICA SHELL
<b>P13</b>	<u>I. Mikalauskaitė</u> , G. Plečkaiytė, K. Paulauskaitė, A. Beganskienė	CONTROLLING UPCONVERSION EMISSION OUTCOME IN Yb <sup>3+</sup> /Er <sup>3+</sup> SYSTEMS
<b>P14</b>	<u>M. Misevicius</u>	LUMINESCENCE OF Eu(II) DOPED AND Dy(III) CODOPED SrAl <sub>4</sub> O <sub>7</sub>
<b>P15</b>	<u>D. Monstvilaite</u> , R. Kaminskas	INFLUENCE OF CALCINED MICA CLAY ON SULFATE ATTACK OF CEMENT STONE
<b>P16</b>	<u>M. Norkus</u> , J.Aglinskaitė, A.Katelnikovas, P.Vitta, R. Skaudžius	ONE-STEP PHOSPHOR IN GLASS SYNTHESIS AND CHARACTERIZATION
<b>P17</b>	<u>A. Pakalniškis</u> , R. Skaudžius	GdPO <sub>4</sub> /Eu/Yb-Tm BASED PHOSPHOR SYNTHESIS AND ANALYSIS
<b>P18</b>	<u>E. Prichockiene</u> , R. Siauciunas	CARBONATION OF α-C2SH AND ITS CALCINATION PRODUCTS
<b>P19</b>	<u>G. Rimkutė</u> , J. Gaidukevič, V. Gurevičienė, J. Razumienė, I. Šakinytė	SYNTHESIS OF THERMALLY REDUCED GRAPHENE OXIDE AND ITS APPLICATION FOR UREA BIOSENSOR WITH IMPROVED LONG-TERM STABILITY
<b>P20</b>	<u>D. Rubinaitė</u> , T. Dambrauskas, K. Baltakys	THE SYNTHESIS OF BELITE–CALCIUM SULFOALUMINATE CEMENT AND ITS PROPERTIES
<b>P21</b>	<u>L. Sinusaite</u> , I. Grigoraviciute-Puroniene, A. Popov, A. Kareiva, A. Zarkov	CONTROLLABLE SYNTHESIS OF TRICALCIUM PHOSPHATE (TCP) POLYMORPHS BY WET PRECIPITATION: EFFECT OF WASHING PROCEDURE
<b>P22</b>	<u>G. Smalakys</u> , R. Šiaučiūnas	THE IMPACT OF RAW MEAL COMPOSITION ON LOW- BASE CALCIUM SILICATE HYDRATES SYNTHESIS
<b>P23</b>	<u>A. Šmigelskytė</u> , Ž. Takulinskas, J. Skirbutas	INFLUENCE OF RAW MEAL COMPOSITION ON SINTERING AND CARBONATION OF CALCIUM SILICATES
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<b>P25</b>	<u>L. Valeikiene</u> , R. Paitian, I. Grigoraviciute-Puroniene, A. Kareiva	SOL-GEL SYNTHESIS OF Mg(X)/AL (X = MN, CO, NI, CU, ZN) LAYERED DOUBLE HYDROXIDES
<b>P26</b>	<u>N. Žmuidzinaučienė</u> , A. Šulčius, E. Griškoniš	CORROSION OF ELECTROLYTIC MANGANESE COATINGS IN 3% NaCl SOLUTION
<b>Organic chemistry</b>		
<b>P27</b>	<u>A. Akmanov</u> , D. Gudeika	ROOM TEMPERATURE PHOSPHORESCENCE OF THIANTHRENE COMPOUNDS
<b>P28</b>	<u>B. Balandis</u> , K. Anusevičius, B. Sapijanskaitė, V. Mickevičius	SYNTHESIS OF NOVEL 1,3-DISUBSTITUTED 5- OXOPYRROLIDINES
<b>P29</b>	S. Grigalevicius, D. Tavgeniene, <u>D. Blazevicius</u> , B. Zhang, S. Sutkuvienė	BIPOLAR PHENOXAZINE-BASED COMPOUNDS AS NEW HOST MATERIALS FOR GREEN PHOSPHORESCENT OLEDs

<b>P30</b>	<u>T Braukyla</u> , R. Xia, M. Daškevičienė, T. Malinauskas, A. Gruodis, V. Jankauskas, C. Roldán-Carmona, C. Momblona, V. Getautis, M. K. Nazeeruddin	HOLE-TRANSPORTING MATERIALS FOR PEROVSKYTE SOLAR CELLS CONTAINING TRÖGER'S BASE CORE AND ENAMINE–LINKED DIPHENYL MOIETIES
<b>P31</b>	<u>V. Dudutienė</u> , A. Zubrienė, J. Kazokaitė, D. Matulis	DEVELOPMENT OF FLUORINATED BENZENESULFONAMIDES AS CARBONIC ANHYDRASE IX INHIBITORS
<b>P32</b>	<u>B. Grybaitė</u> , R. Vaickelionienė, V. Mickevičius	SYNTHESIS OF NOVEL N-ARYL-N-POLYSUBSTITUTED THIAZOLYL- $\alpha$ -ALANINES
<b>P33</b>	<u>M. Iškauskienė</u> , A. Urbonavičius, G. Ragaitė, M. Dagilienė, F. A. Sløk, A. Šačkus <sup>1,2</sup>	SYNTHESIS AND STRUCTURE DETERMINATION OF ALKYL N-(N-Boc-PIPERIDINYL)PYRAZOLECARBOXYLATES
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<b>P39</b>	<u>A. Klevinskas</u> , I. Tumosiene, I. Jonuškienė, K. Kantminienė	SYNTHESIS OF SHIFF BASES FROM 3-[(4-METHOXYPHENYL)AMINO]PROPANEHYDRAZIDE AND THEIR ANTIBACTERIAL ACTIVITY
<b>P40</b>	C.-W. Liao, Y.-C. Hsh, C.-C. Chu, C.-H. Chang, <u>G. Krucaite</u> , D. Volyniuk, J. V. Grazulevicius, S. Grigalevicius	AGGREGATION-INDUCED EMISSION TETRAPHENYLETHENE TYPE DERIVATIVES FOR BLUE TANDEM ORGANIC LIGHT-EMITTING DIODES
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**POSTER SESSION II****16:00 – 17:00****Analytical chemistry**

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<b>P54</b>	<u>E. Dauksaite</u> , A. Ramanaviciene, A. Kausaite-Minkstimiene	SURFACE PLASMON RESONANCE IMMUNOSENSORS FOR HGH DETECTION
<b>P55</b>	<u>V. Kavaliauskas</u> , A. Žilionis	DETERMINATION OF PHTHALATES IN BOTTLED WATER BY ULTRA-HIGH PRESSURE LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY
<b>P56</b>	<u>V. Lisyte</u> , B. Brasiunas <sup>1</sup> , A. Popov, A. Ramanaviciene	GLUCOSE BIOSENSOR BASED ON GLUCOSE OXIDASE AND POLYANILINE NANOFIBERS

**Applied chemistry**

<b>P57</b>	<u>O. Aleknavičiūtė</u> , R. Baranauskienė, P. R. Venskutonis	FRACTIONATION OF HEMP EXTRACTS BY USING SUPERCRITICAL CARBON DIOXIDE AND CO-SOLVENT ETHANOL
<b>P58</b>	<u>G. Aleliūnaitė</u> , R. Baranauskienė, E. Dambrauskienė, P.R. Venskutonis	AROMA PROFILE AND TOTAL PHENOLICS IN LEMON BALM AND WHITE HOREHOUND ESSENTIAL OILS AND WATER EXTRACTS
<b>P59</b>	<u>A. Banytė</u> , R. Baranauskienė, R. Žvirdauskienė, P.R. Venskutonis	AROMA PROFILE, TOTAL PHENOLICS AND ANTIMICROBIAL ACTIVITY OF SPEARMINT AND PEPPERMINT ESSENTIAL OILS AND WATER EXTRACTS
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<b>P61</b>	<u>K. Dabrovolskas</u> , G. Krucaite, E. Skuodis, I. Jonuskiene, D. Gudeika	SYNTHESIS AND ANTIMICROBIAL ACTIVITIES OF CARBAZOLE-BASED COMPOUNDS
<b>P62</b>	<u>N. Dukštienė</u> , V. Krylova	MORPHOLOGY OF POLYAMIDE 6/Se-S-Cd-Ag COMPOSITE MATERIALS
<b>P63</b>	<u>G. Gaidamavičienė</u> , A. Žalga	CHARACTERIZATION OF La <sub>1.9</sub> Ca <sub>0.1</sub> Mo <sub>2</sub> O <sub>8.95</sub> CERAMICS SYNTHESIZED BY THE AQUEOUS SOL-GEL METHOD
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# Invited speakers

## Information about the authors

### **Prof. dr. Ismail Hakki Boyaci**



Ismail Hakki Boyaci is professor in the Department of Food Engineering at Hacettepe University, Ankara, Turkey. Professor Boyaci graduated in 1995 with food engineering degree, and gained his PhD in 2001. Professor Boyaci received his PhD by working on the development of biosensor for multiple detections. He is a research fellow in Faculty of Mathematic and Physic, Charels University, Czech Republic in 1997. He also, worked as a post doctoral research fellow on microbial immunosensors in the group of Prof. Dr. William R. Heineman at the Chemistry Department, Cincinnati Univeristy, OH, USA. His research interests include biosensors based on optical and electrochemical sensor and development of different spectroscopic techniques for food analysis mainly on Raman, SERS, NIR and LIBS. He has published more than 150 papers among peer-reviewed journals. He has completed 8 book chapters and 6 patents.

Talk Title: Raman and SERS–based detection of Gene and Microorganisms

### **Prof. dr. Sheng-Tung Huang**



Sheng-Tung Huang currently is a distinguished professor at Institute of Biochemical and Biomedical Engineering in National Taipei University of Technology (TAIPEI TECH). After graduating from the University of California, Riverside with Bachelor's and Master's degrees in Biochemistry, Sheng took up doctoral work in the new direction of synthetic organic chemistry at Brandeis University. Upon receiving his PhD in Bioorganic Chemistry in 1998, he undertook the position of a medicinal chemist at a leading Taiwan pharmaceutical company, Scinopharm. In 2000, Sheng taught in the capacity of an assistant professor and associate professor at the Department of Biochemistry in Taipei Medical University. He joined the Department of Chemical Engineering and Biotechnology at National Taipei University of Technology (TAIPEI TECH) in 2005, where he later became a full professor. He had served as the Chair of Institute of Biotechnology and as the Dean of International Affairs, and he is currently the Dean of Academic-Industrial Cooperation at TAIPEI TECH. His research interests include developing innovated fluorogenic and electrochemical active molecules for biosensors, bioelectronics and bio-imaging, synthesizing novel anti-cancer agents, design and synthesizing DNA intercalators for electrochemical gene detection and preparing new efficient water vapor impermeable packaging materials for new generation of bendable solar cells and bio-electronic devices.

Talk title: Design Strategies and Applications of Self-Immolative Chemical Probes for Biosensing

### **Prof. dr. Fabio Marchetti**



Fabio Marchetti received a M.Sc. degree in chemistry (1991) and a Ph.D. in inorganic chemistry with Prof. A. Cingolani at the University of Camerino (Camerino, Italy, 1996). Then he joined the University of Camerino as a Researcher, in 2002 he was an Associate Professor and in 2011 he became Full Professor of General and Inorganic Chemistry at the School of Science and Technology, University of Camerino, Italy. His main research interests are in coordination and bioinorganic chemistry of biologically active metal complexes of pyrazole-based ligand and their possible applications in medicinal and composite materials chemistry. Fabio Marchetti is author and co-author of more than 200 papers in international peer-review journals, including 8 invited reviews, of 4 patents (2 international) and more than 180 communications to national and international congresses.

**Talk Title:** Novel composite materials for antimicrobial applications

### **Prof. dr. Zineb Mekhalif**



Zineb Mekhalif was born in Sétif (Algeria) in 1966. She got her first higher education degrees from the University of Sétif. She moved to France in 1989 and obtained her PhD degree in 1994 from the University of Pierre & Marie Curie (Paris) in Electrochemistry in the research field of conducting polymers. She joined the University of Namur in 1995 for a post-doctoral research position in surface chemistry. She got a permanent position at the University of Namur in 1998 as Professor. She is currently the director of the Laboratory of Chemistry and Electrochemistry of surfaces (CES). Her research interests are the design and elaboration of surface and interfacial materials (thin and ultra-thin organic and inorganic films on metal, oxide and polymer substrates) by chemistry processes (electrochemistry, self-assembly, sol-gel film deposition). The goal is to obtain structured surface materials with new and/or improved properties resorting to the bottom-up approach, which depends on the control of processes and interactions at the molecular level. Main topics are: Molecular self-assembly on active metals, carbon nanotubes functionalisation for composites elaboration (polymers/CNTs, metal or metal oxides/CNTs), surface modification for biomaterials applications, electrodeposition in ionic liquids. She published more than 170 papers and 6 patents, supervised 19 PhDs, 50 Masters and 16 Post-Docs.

**Talk title:** Electrochemistry and Surface Chemistry: a powerful combination for nanotechnology.

## Dr. Magdalena Oćwieja



Magdalena Oćwieja is a member of the Group of Colloids from the Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences. She is a chemist (MSc at the Jagiellonian University (2009), PhD at the Institute of Catalysis and Surface Chemistry PAS (2013)) specialized in the physicochemistry of metal nanoparticles. The scientific research of M. Oćwieja is focused on the mechanisms and adsorption kinetics of colloid particles at solid/liquid interfaces, especially the electrostatic interactions between nanoparticles and surfaces which determine the stability of colloid monolayers obtained in the self-assembly processes. She has a wealth of experience in the studies of the influence of silver nanoparticle surface properties on their biological activity. The results of Dr. Oćwieja's works have been published in 50 articles in international journals of world-wide circulation.

**Talk Title:** Noble metal nanoparticle layers of tunable coverage, structure and charge



## **Abstracts of invited speakers**

## RAMAN AND SERS-BASED DETECTION OF GENE AND MICROORGANISM

**Ismail Hakki Boyacı \***

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Detection of microorganisms and genetically modified organisms (GMO) has an increasing impact in terms of food safety and human health. Over the years, different approaches have been used to determine the major pathogenic bacteria, which can cause severe illness and possible death. Therefore, studies on developing reliable, sensitive and rapid methods for detection of pathogenic bacteria are on the increase. Several techniques have been developed for specific detection of foodborne pathogens such as automated or modified conventional assays, biosensors, immunological methods or nucleic acid based assays. On the other hand, GMO detection are gaining worldwide attention, especially in molecular biology and clinical diagnostics. Detection and identification of GMO have been achieved by using DNA and protein-based methods. In both cases, conventional methods have certain disadvantages in terms of analysis, sample preparations, selectivity, quantitative results, etc. At this point, Raman and SERS can an attractive alternative to determine pathogenic bacteria and GMO. Here, different applications of Raman and SERS will be presented to evaluate its potential to be used as rapid and sensitive method for detection of pathogenic bacteria and GMO. At first, the performance of Raman spectroscopy to identify *Pseudomonas aeruginosa* and *Pseudomonas fluorescens* was evaluated. As a result, Raman spectroscopy accompanied with principal component analysis accomplish to differentiate the two most dominant accompanying flora among pathogen *Pseudomonas* species. An alternative cultivation-free verification method with 15 min analysis time was developed. Later on, the potential of the SERS method to detect *Escherichia coli*, 35S promoter gene and GMO was evaluated. As a result, a successful sandwich immunoassay method for *Escherichia coli* detection was developed using SERS. On the other hand, SERS with rolling circle amplification method used to determine 35S promoter gene for GMO and detection the detection limit was found to be 0.1pM. In a different study, multilayered SERS platform was developed to determine GMO and detection limit was found to be 34 fM. As a result, Raman and SERS based methods showed they can be used as rapid, selective and sensitive method for detection of pathogenic microorganisms and GMO.

# DESIGN STRATEGIES AND APPLICATIONS OF SELF-IMMOLATIVE CHEMICAL PROBES FOR BIOSENSING

**Sheng-Tung Huang**

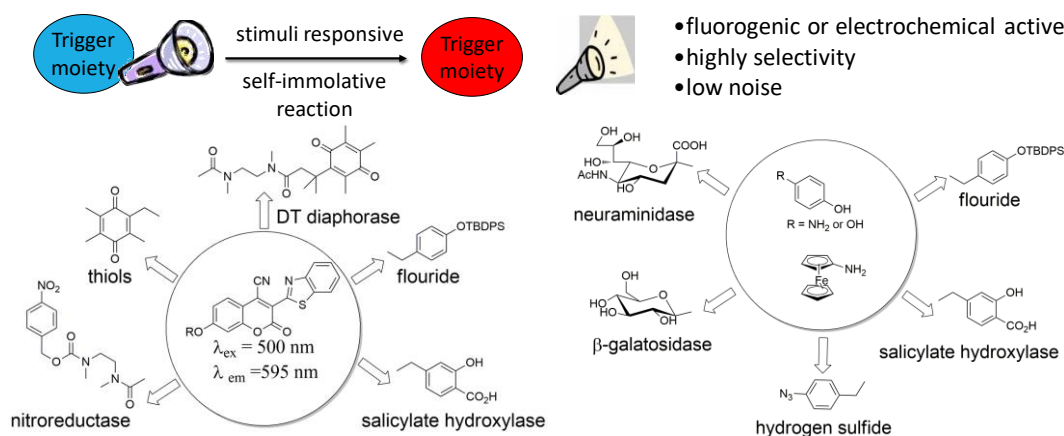
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The biosensor field is largely depending on the use of bio-recognition agents such as enzymes, proteins, antibodies or aptamers etc. Irrespective of high selectivity, their high production cost and instability are key limiting factors that hindering the applicability of biological receptors toward next stage of biosensor development. Our lab research is focused on circumventing this issue by designing a novel class of stimuli-responsive chemical probes that are either fluorescent or electrochemical. They are highly selective and reveal their signaling properties only by a specific user-designated chemical reaction. These biomimetic probes are highly stable at room temperature for several months, readily produced in large scales at low-cost, and amenable for easy storage and transportation. Our research over the past years indicating that these potential substrates are robust alternative to the fragile biological receptors, without compromising selectivity and sensitivity. Design and synthesis of such stimuli-responsive latent probes and applying them as the analytical tool for analytes detection are ongoing research efforts in my research group. Design strategies and applications of several latent fluorogenic and electrochemical probes which were completed by our group will be introduced in this talk.

## Self-immolative Responsive Probe



## NOVEL COMPOSITE MATERIALS FOR ANTIMICROBIAL APPLICATIONS

**Prof. Fabio Marchetti**

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ITALY*

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Microbial contamination of polymeric materials plays an important role in the transmission of infectious diseases. In response to the microbial challenges, the development of antimicrobial plastics is attracting an increasing interest for potential applications in many fields of modern society. The most investigated approaches to the design and production of antimicrobial materials are based on silver or zinc oxide nanoparticles, however the use of nanoparticles has been also pointed out as a source of pollution with potential health risks, with consequences that today are mostly unexplored. Research carried out in our lab has recently focused to alternative pathways to produced efficient antimicrobial composite materials, based on easily up-scalable embedding procedure of silver(I) and copper(II) coordination polymers as efficient additives during the extrusion process to different polymeric matrixes, such as polyethylene and polyvinyl chloride.

Alternative antimicrobial composite materials have been also developed by combining the porosity of carbon materials derived from agricultural waste residues (almond shells) and the antimicrobial activity of half sandwich (arene)Ru(II)-curcumin complexes. These carbon composites can find application in air filters or aqueous treatment devices. New directions and strategies in this research field will be discussed.

## **ELECTROCHEMISTRY AND SURFACE CHEMISTRY: A POWERFUL COMBINATION FOR NANOTECHNOLOGY**

**Zineb Mekhalif**

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Belgium*

Modification of surfaces with thin or thick layers, organic, inorganic or hybrids is nowadays a powerful and efficient approach to provide new functionalities to materials making them attractive in many domains of applications.

Electrochemical modifications of surfaces through oxidation or reduction to elaborate organic monolayers, multilayers, polymers, metals, alloys and composites on surfaces concern many fields such as :

- Electrochemical pretreatment of metallic surfaces
- Electropolishing
- Electro-assisted adsorption of organic molecules
- Electropolymerisation
- Electrodeposition
- Electrochemical analyses...

In this presentation, few illustrative examples from the above ongoing research projects in our laboratory will be discussed to highlight the use of electrochemistry to modify surfaces of active metals and to elaborate new nanomaterials.

# NOBLE METAL NANOPARTICLE LAYERS OF TUNABLE COVERAGE, STRUCTURE AND CHARGE

**M. Oćwieja\***, Z. Adamczyk, D. Lupa, J. Maciejewska-Prończuk, M. Morga,  
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The methods of preparation of nanoparticle mono- and multilayers of controlled coverage, structure, electrokinetic properties and stability are continuously developed in order to apply them for the formation of efficient catalysts, biologically active substrates as well as plasmonic, piezoelectrical and electrochemical sensors. Among numerous physical and chemical methods dedicated for the formation of noble metal nanoparticle layers, the electrostatically-driven self-organization of nanoparticles at solid/liquid interfaces is the most common. In our studies we proved that using stable colloidal suspensions of controlled ionic strength and pH one can prepare well-defined mono- and multilayers on substrates oppositely charged to nanoparticles [1]. However most of such substrates were characterized by negative surface charge similarly as noble metal nanoparticles synthesized via a chemical reduction method with the use of low molar mass compounds. Owing to this fact, the electrostatically-driven deposition process was preceded by the modification of the solid substrates by cationic polyelectrolytes or proteins [1].

Our studies revealed also that the presence of such organic anchoring layers affects morphology and stability of metal nanoparticle layers in some cases strongly limiting their usefulness. Therefore it was obvious that the elimination of organic anchoring supports and use of positively charged noble metal nanoparticles for formation of their layers on solid surfaces is more promising approach taking into account their potential applications.

Our further studies showed that using positively charged gold and silver nanoparticles, stabilized by cysteamine or cysteine, one can produce on solid substrates well-defined mono- and multilayers under both diffusion and flow conditions [2,3]. The kinetics of nanoparticle deposition was studied applying gravimetric methods (QCM), streaming potential measurements and microscopic imaging (TEM, SEM). The experimental results were interpreted in terms of theoretical models. Obtained outcomes allowed to conclude that increasing ionic strength up to the range of the nanoparticle stability one can tune coverage, structure and roughness of formed layers. It was also found that monolayers formed from cysteine-stabilized nanoparticles exhibited interesting pH-dependent electrokinetic properties [3]. It was determined that at pH lower than 5.0 such monolayers exhibited positive zeta potential whereas above this value they were characterized by negative zeta potential increasing with ionic strength. The streaming potential measurements showed that in spite of the inversion of sign of the zeta potential, the monolayers were characterized by a high stability. Application potential of such noble metal nanoparticle layers was proved in the studies on their biological activity towards tumor cells and in sensing of organic compounds with the use of surface enhanced Raman spectroscopy (SERS).

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**General session**  
**Oral presentations**

# ENZYME INHIBITORY ACTIVITY OF HYDROETHANOLIC EXTRACT OF YAM (*DIOSCOREA CAUCASICA* LIPSKY) LEAVES

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The concept of food as a medicine is one of the main trends in modern nutrition, particularly in the age of increasing role of functional foods and nutraceuticals. Therefore, plant bioactive compounds are considered as important nutrients with health beneficial and therapeutic potential for preventing and treating various ailments, including chronic hyperglycemia. Chronic hyperglycemia is rather dangerous for human health, particularly because it is asymptomatic during the initial periods of development, while over several years it may result in long-term damage or dysfunction of multiple organs, including kidneys, eyes, nervous and cardiovascular systems. It also increases the risk of the development of diabetes mellitus and microvascular complications and may reduce life expectancy. Therefore, the foods with effective pancreatic  $\alpha$ -amylase inhibitors are considered as an effective strategy to lower the levels of postprandial hyperglycemia *via* control of starch breakdown. This study aimed at evaluating enzyme inhibitory activity of yam leaf extracts.

**Materials and methods:** Dried yam (*Dioscorea caucasica* Lipsky) leaves were donated by Kaunas Botanical Garden of Vytautas Magnus University. Plant material was ground and 20.0 g of the powder were extracted with 200 mL 70% (v/v) ethanol in a rotary shaker (200 rpm) for 1 h. The extract obtained was filtered through Whatman filter paper and the solvent was removed at 40 °C in a rotary vacuum evaporator (ethanol) and freeze-dryer (water). The extracts were tested for their  $\alpha$ -amylase inhibitory activity at the concentrations of 0.5, 1.0, 2.0, 2.5 and 5.0 mg/mL using 3,5-dinitrosalicylic acid and starch as a substrate [1, 2].

**Results:** Hydroethanolic extracts of yam leaves inhibited  $\alpha$ -amylase in the dose dependent manner in the concentration range of 0.5 – 2.5 mg/mL (from 2.2 to 45.31%). Higher extract concentrations did not increase enzyme inhibition. Acarbose, which was tested as a positive control at the concentration of 0,05 mg/mL inhibited 93.83% of enzyme. Consequently, *D. caucasica* leaves contain phytochemicals, which inhibit amylolytic enzyme, e.g., as it was previously reported for another *Dioscorea* species by Ghosh et al. [3]. Preliminary screening of hydroethanolic extract of yam used in our study was performed by ultra high performance chromatography – time-of-flight-mass spectrometry.

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# ANTIOXIDANT CAPACITY AND PHYTOCHEMICAL COMPOSITION OF GUELDER-ROSE BERRY POMACE EXTRACTS

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Guelder-rose (*Viburnum opulus*) berries are not consumed as fresh fruits due to unacceptable sensory properties, however they are processed into jams and juice, which may be used as ingredients in other products [1]. It has already been shown that juice pressing by-products (when discarded – waste) are suitable for developing new functional ingredients; their efficient processing also diminishes waste treatment and disposal costs and generates extra value by commercialization of new materials for foods, nutraceuticals and other applications [2]. In general, development of effective waste treatment processes and their return into the production chain plays an important role in fulfilling the tasks of circular bio-economy [3].

In this study guelder-rose berry pomace were dried, ground and extracted by conventional and innovative high pressure extraction techniques using one step and sequential extraction procedures with various polarity solvents. The antioxidant capacity of lipophilic fractions were tested in Rancimat and Oxipress apparatus, while hydrophilic fractions were evaluated by total phenolic content (TPC) and ABTS<sup>•+</sup>/DPPH<sup>•</sup> radical scavenging assays. The composition of extracts obtained was analysed by UPLC-Q/TOF-MS and GC-MS.

In Oxipress and Rancimat assays the concentrations of 0.5, 1.0 and 1.5 % of *V. opulus* berry oil were used: only at the highest concentration applied weak antioxidant effect was observed. The dominant compounds in *V. opulus* hydrophilic extracts were procyanidin B2, catechin, rutin, chlorogenic, quinic and malic acids, while the composition of oily fraction was rich in oleic (C18:1, n-7) and polyunsaturated linolenic (C18:3, n-3) and linoleic (C18:2, n-6) fatty acids. Consequently, triacylglycerols in lipophilic fraction were composed mainly of above-mentioned unsaturated fatty acids. Generally, this study has shown that *V. opulus* berry pomace contains valuable bioactive compounds, which may be efficiently recovered by extraction and the extracts obtained considered as promising materials for the development of functional ingredients for foods and nutraceuticals.

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## RARE EARTH ELEMENTS: INDUSTRIAL APPLICATIONS

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Rare earth elements and their ions possess unique chemical and physical properties. Therefore, they are widely applied in various household and industrial devices. Many of us might even be unaware that one or the other devices that we use on the daily basis contain rare earth elements or their ions. For example, many of us cannot imagine the life without music and high quality head- or ear- phones that contain strong neodymium based magnets. These magnets are very strong; thus high quality products can be made smaller. Another application of these magnets are wind turbines, what makes them more powerful. Cerium ( $\text{Ce}^{3+}$ ) and europium ( $\text{Eu}^{2+}$ ) ions are found in white light emitting diodes (wLEDs) used for illumination as well as fluorescent lamps used for tanning. Moreover,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  are used in fluorescent (FL) and compact fluorescent (CFL) lamps. The presentation will overview the most important areas, where rare earth elements and their ions are applied.

# PENETRATION OF TITANIUM INTO ALUMINA NANOPORES AFTER ATOMIC LAYER DEPOSITION OR MAGNETRON SPUTTERING

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Titanium oxides can act as protective, anti-frictional layers on various substrates [1]. Recently it was reported that nanothin Ti layers can significantly reduce friction on anodized alumina [2]. In this study nanothin Ti and TiO<sub>2</sub> layers were deposited on anodized Al alloys and their penetration into the nanopores was characterized by X-ray photoelectron spectroscopy (XPS) and Energy Dispersive X-ray spectroscopy (EDX).

Anodization of 1050 of 99.67% purity and 6082 of 96.72% purity Al alloys was performed in the sulfuric/oxalic electrolyte to produce Al<sub>2</sub>O<sub>3</sub> coatings of 60 μm thickness. Nanothin Ti layers of 16 nm thickness were deposited by magnetron sputtering and their SEM recorded as described previously [2]. Alternatively, TiO<sub>2</sub> layers of 15 nm thickness were formed by a two-pulse process based on Tetrakis (dimethylamino) titanium (99%, Merck) chemisorption and its hydrolysis into TiO<sub>2</sub> using Atomic Layer Deposition (ALD) system Fiji F200 (Cambridge NanoTech). In ALD, coatings were heated to 250 °C at 30–35 Pa vacuum. Ti (deposited with magnetron) and TiO<sub>2</sub> (deposited with ALD) layers were analysed by XPS ESCALAB-MKII (VG Scientific, UK). Non-monochromated Mg K (1253.6 eV) anode was used for photoelectron excitation powered at 15 kV and 20 mA. Etching with Ar<sup>+</sup> ions was performed at ~5·10<sup>-4</sup> Pa using a 3 kV energy at ~60° ion beam and 20 μA/cm<sup>2</sup> current density. The depth of ~90 nm was achieved after 1800 s. EDX analysis was performed using INCA spectrometer (Oxford Instruments, UK).

SEM images revealed that TiO<sub>2</sub> layers, deposited by ALD, completely covered the nanopore openings, while sputtering of Ti layers appeared uniform only on 1050 alloy, Fig. 1.

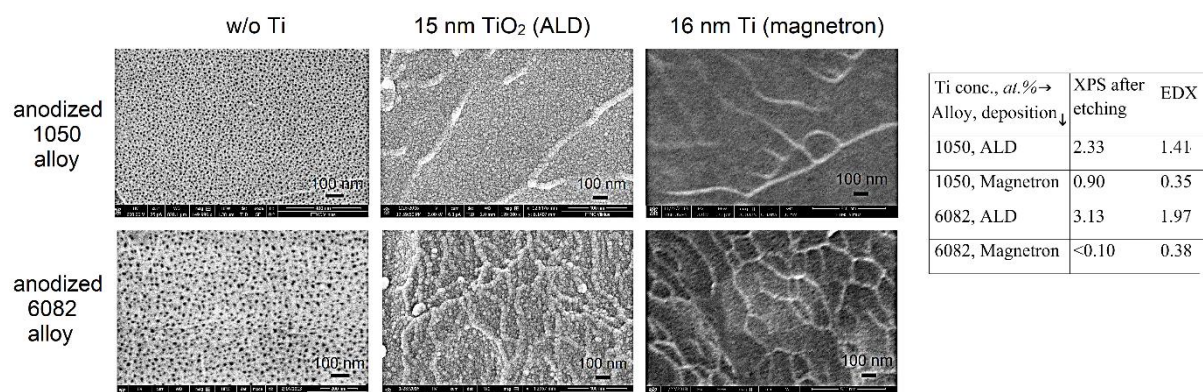


Fig. 1. SEM images before and after deposition of 15 nm TiO<sub>2</sub> (ALD) or 16 nm Ti (magnetron) layers on anodized alloys (left) with measured Ti contents by XPS after etching to ~90 nm and by EDX (right).

Elemental analysis showed that despite of wider nanopores in 6082, Ti contents were quite low at 0.1 μm or deeper. In contrast, ALD assured deeper penetration of Ti into nanopores than magnetron sputtering, which implies more benefits to technical performance.

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## IT'S NOT WHAT WE KNOW – IT'S HOW WE THINK

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In 1993 I (with my students) started Advanced Chemistry Development, Inc. (ACD/Labs), one of the first chemistry informatics companies helping pharma and chemical industries to develop new compounds. Since then I learned few things which I want to share.

Life and science are governed by similar principles that differ a lot from what we are taught in universities. Chemistry is closest not to theoretical physics and math (as they are presented in textbooks), but to "practical psychology". True chemist is also true mystic and alchemist. The only universal law in the Universe is the Law of Unity of Opposites. It states that (i) those who fight will eventually unite; (ii) each equilibrium leads to new kinetics; (iii) entropy measures higher intellectual dimensions rather than disorder and chaos; (iv) the real power is in softness and subtleness rather than brutal action, categorical thinking and postulating; (v) the real purpose of science is not to acquire new data or facts, but to lift ourselves to higher dimension from where complex phenomena look natural, whereas natural numbers look complex (consisting of imaginary and real parts). What matters is not what we think or do, but how we think or do. Never rush to the goal, but rather let the compound interest ("snowball") effect do the job for you. Revolution is made in small bits everyday, provided that you like what you do.

The higher the number of simultaneously acting forces ("process development dimension"), the lower the required total energy. Therefore always pursue a "wholistic" approach, insisting that life consists of two parts - one understandable and visible, another mysterious and invisible. Never be dogmatic, accept all ideas and events what come to you and release all what has to go. Then you will see an immense beauty in uniting science with poetry, and exoteric with esoteric. You will understand why optimists and pessimists often arrive at different outcomes, and why it is better to think of atoms and molecules as live creatures with whom you can talk to, rather than dead objects that are indistinguishable from each other...

You will see that your own thoughts and feelings shape the "objective reality". Many paradoxical examples will uncover in new light - e.g., colloidal "polywater" of Fediakin and Deriagin; "water memory" of Jean Batista; Morphogenetic Fields of Rupert Sheldrake, consciousness affecting matter of Dean Radin, conscious cells of Bruce Lipton, quantum reality of Lothar Schafer

# DETERMINATION OF STORAGE CONDITIONS OF REFINED RAPESEED OIL FORTIFIED WITH PHENOLIC ACID ESTERS

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Rapeseed oil is the most used vegetable oil in Poland. It has a lot of bioactive compounds such as: polyphenols, tocopherols, sterols and carotenoids with health beneficial properties and high nutritional value due to a unique fatty acid composition (SAFA – 7%, MUFA, n-9 – 63% and PUFA, n-6 19% and n-3 – 9%) [1].

Unfortunately, more of the bioactive compounds remain in rapeseed cake and meal. Only small amounts of bioactive components are transferred to the crude oil during technological process, however refining causes further their decrease and reduce oil's quality [1, 2].

Therefore, synthesis of a new liposoluble antioxidants plays important role in oil industry. Antioxidant activity of phenolic acid esters (phenolipids) depends on their chemical structures (number and distribution of hydroxyl and methoxyl groups) and length of alkyl chains [3].

Under storage conditions during contact with air, temperature and light, oxidation processes in oils undergo, especially after opening the bottle. Unfortunately, unsaturated fatty acids react with oxygen in closed storage bottle, also [4]. Therefore oil's supplementation is necessary.

In the present study, phenolic acid ester - octyl sinapate was synthesized by modified Fischer esterification. Oils were fortified with this ester at different concentration ranges and kept under various conditions. Additionally, rapeseed oil was supplemented with synthetic phenolic antioxidant butylated hydroxyanisole (BHA). Oxidation parameters such as: acid value, anisidine value, peroxide value and content of conjugated diene and triene of the fortified oils before and after storage were determined. Moreover, antioxidant capacity after storage at different conditions was evaluated by four modified analytical methods: ABTS, DPPH, FRAP, Folin–Ciocalteu.

Oxidation parameters depended on the oil storage location and concentration and type of added antioxidants. Dark place and low temperature did not affect significantly the oxidative stability of the fortified oils. However, antioxidant capacity of the enriched oils before and after storage were higher in comparison with non-supplemented oil. Storage process, especially exposition on light caused decrease of antioxidant activity for 70% for non-supplemented oil. On the other hand, increase in antioxidant potential for the supplemented oil with 5000 ppm octyl sinapate was observed.

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# FAST FOURIER TRANSFORM ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY FOR MONITORING SURFACE MODIFICATION

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The most recent advances in the development of electrochemistry enabled the development of fast Fourier transform electrochemical impedance spectroscopy (FFT-EIS) [1, 2]. FFT-EIS is one of the fastest and the most informative electrochemical techniques, which in very short period of time can provide EIS spectra. Therefore, FFT-EIS is very useful for the investigation of very dynamic electrochemical systems and for monitoring in real time formation of various layers on different surfaces [3-6].

FFT impedance spectrometer was constructed by professor Georgi Popkirov who developed and advanced FFT EIS based technique together with prof. R. N. Schindler in 1990 [1, 2]. In this technique, system is perturbed not by the consequently applied sine waves of different frequencies, but by the superposition of 30-50 sine waves with properly chosen frequencies. If frequency range from 1.5 Hz to 50 kHz is applied, then the measurement time is just 0.67 s. It is a big advantage of this technique to acquire EIS spectra many times faster in comparison with conventional EIS based techniques.

A significant advantage of FFT-EIS spectrometer is that it is easily controlled. All “bad” data points can be controlled/avoided. All information we need is presented on the screen and everyone who measures impedance spectra can see “good” or “bad” measurement is performed. If we see a lot of red lines on the screen, we should improve quality of the measurement (remove bubbles on the electrode, check reference electrode, wires parasitic capacitances and other). EIS data then are calculated into real and imaginary parts of impedance and presented in Nyquist plot. Also, there is possibility to plot data in Bode coordinates, and even to calculate EIS parameters by fitting data using simple Randles’ circuits.

The biggest advantage of FFT-EIS equipment is fast measurement and data validation by easily controlling and avoiding bad data points.

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# Poster presentations

# ROOM TEMPERATURE PHOSPHORESCENCE OF THIANTHRENE COMPOUNDS

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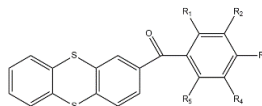
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Room-temperature phosphorescence (RTP) has attracted a great deal of attention in the fields of optoelectronic devices [1], high contrast bio-imaging [2], photodynamic therapy [3], photocatalytic reactions [4], and oxygen indicators [5]. Heavy-metal complexes such as iridium complex are commonly used for room temperature phosphorescence but their potential toxicity and instability particularly in case of blue phosphors still remain to be solved. Room temperature phosphorescence from metal-free organic phosphors has attracted much attention in recent years since metal-free phosphors were presented as bright as organometallic compounds, quantum dots, and fluorescent molecules at room temperature [6].

Thianthrene being an electron-donor with a stable mono- and bicationic forms [7,8] has been used in several materials, including small molecules [8,9]. In particular, phosphorescent properties of thianthrene crystals have already been demonstrated [11], but no study has been performed on its derivatives. Of particular interest are the room temperature phosphorescent (RTP) properties of thianthrene, which suggests this group can be used to promote dual fluorescence-phosphorescence at room temperature in its derivatives.

In this study we present the synthesis of thianthrene derivatives (figure 1) examining the effect of the type of substituent on their RTP properties. The aim of the study is to understand structural and electronic effects, such as produced steric hindrance properties of benzoyl chloride substituents on thianthrene.



Compound	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
R1	H	F	H	H	Br	H	Cl	Cl	Cl	H	F	F	F	H	H
R2	H	H	F	H	H	H	Cl	H	H	Cl	H	H	H	F	F
R3	H	H	H	F	H	Br	H	F	H	F	F	H	H	F	H
R4	H	H	H	H	H	H	H	H	H	H	H	F	H	H	F
R5	H	H	H	H	H	H	H	H	F	H	H	H	F	H	H

**Figure 1.** Thianthrene molecular structures studied in this work.

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# FRACTIONATION OF HEMP EXTRACTS BY USING SUPERCRITICAL CARBON DIOXIDE AND CO-SOLVENT ETHANOL

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**Introduction.** Supercritical fluid extraction (SFE) is a green technology, which is frequently used for obtaining solvent-free extracts from various plant materials. Carbon dioxide (CO<sub>2</sub>) is the most widely used solvent in SFE, due to its availability, low price, safety and non-toxicity. However, SFE-CO<sub>2</sub> dissolves the waxes, which are not desirable substances in the extract [1]. The main task of this study was to develop a process enabling to obtain the fraction with the increased concentration of the target hemp compounds, namely terpenes and cannabinoids (T/C).

**Materials and methods.** SFE-CO<sub>2</sub> was performed in a *Helix* extractor with 500 cm<sup>3</sup> vessel using two separators, S<sub>1</sub> and S<sub>2</sub>. The possibilities of fractionating hemp extracts were tested by maintaining S<sub>1</sub> at 7 MPa and different cooling temperatures (-30 – 0 °C) in order to separate waxes from other (mostly volatile) compounds, which were expected to be collected in the S<sub>2</sub>. Pure CO<sub>2</sub> and its mixture with a co-solvent ethanol, introduced into the solvent flow at the level of 2.0 mL min<sup>-1</sup> (5% EtOH), were tested at the same separation parameters.

**Results.** The yields of wax fractions after SFE-CO<sub>2</sub> fractionation, depending on S<sub>1</sub> temperature, was 6.6 – 10.6 times higher than the yield of T/C fractions in the S<sub>2</sub>. On the contrary, SFE-CO<sub>2</sub>/5% EtOH resulted in 1.6 – 2.3 times higher yields of T/C fractions, than those of wax fractions. The most efficient separation was achieved at -10 °C; the yield of T/C fraction reached 3.15%. The main volatile components in this fraction, identified and quantified by GC×GC-TOF/MS and GC-FID, respectively, were β-caryophyllene (6.52%), α-humulene (2.03%), β-farnesene (0.89%), caryophyllene oxide (0.97%) and phytol (3.94%). The highest concentrations of the main cannabinoids, namely cannabidiol (CBD) and cannabidiolic acid (CBDA), determined in *C. sativa* fractions by HPLC-UV, after SFE-CO<sub>2</sub> were 14.17% (-30 °C, pure CO<sub>2</sub>) and 17.66% (-30 °C, 5% EtOH), respectively. However, the biggest recoveries of CBD and CBDA were obtained at -10 °C with 5% EtOH, 0.29 and 0.53 g/100 g dry weight, respectively. Antioxidant potential indicators of the extracts and solid materials assessed by total phenolic content (TPC), ABTS<sup>•+</sup> scavenging and oxygen radical absorbance capacity (ORAC) assays varied in a wide range. The highest ORAC values were determined for T/C fractions obtained at -10 °C during SFE-CO<sub>2</sub> and SFE-CO<sub>2</sub>/5% EtOH, 987.73 and 873.02 mg trolox equivalents (TE)/g extract, respectively. However, the recovery of antioxidants was remarkably higher when 5% EtOH was applied, 27.50 vs 3.06 mg TE/g DW, respectively.

**Conclusion.** Efficient separation of terpenes and phytocannabinoids from waxes may be achieved by SFE-CO<sub>2</sub> with addition of 5% co-solvent EtOH: the highest yield of T/C as well as the strongest antioxidant capacity was achieved using -10 °C for separating crude extract.

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## WHITE HOREHOUND ESSENTIAL OILS AND WATER EXTRACTS

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Aromatic and spicy herbs due to their flavouring properties, antimicrobial activity and health benefits have been used in culinary and folk medicine applications since ancient times. Lemon balm (*Melissa officinalis*) and white horehound (*Marrubium vulgare*) essential oils (EO) and water extracts (WE) are known as a good source of important biologically active plant metabolites possessing antioxidative, antimicrobial, anticancer, antiinflammatory, antidepressant, antihypertensive and hypoglycemic activities. The aim of this study was to evaluate chemical composition and aroma profile of lemon balm leaves (MO), horehound leaves (MV-L) and stems (MV-S), and to determine the total phenolic content (TPC) in EOs and WEs. The aroma profile of leaves (L) and stems (S) was analysed by static headspace solid phase microextraction (HS-SPME) and gas chromatography time-of-flight mass spectrometry (GC-TOFMS). The EOs were hydrodistilled (HD) in a *Clevenger* type apparatus and further analysed by GC-TOFMS. TPC was determined by Folin–Ciocalteu method and expressed in gallic acid equivalents in dry extract weight (mg GAE/g edw).

MV- S/L and MO contained 8.1/8.5 and 10.9% water, 6.1/9.3 and 6.5% ash, 1.5/2.6 and 1.9% lipids and 11.7/13.2 and 29.2 mg/100g vit.C. The yields of EO varied from 0.03 (MV-S) to 0.1% (MO/MV-L). The residues after HD were separated into liquid and solid fractions by filtration. The liquid fractions were lyophilized and spray dried into WE<sub>L</sub> and WE<sub>S</sub>, yielding 25.0% (MO) and 44.4% (MV-L) and 39.6% (MO) - 64.5% (MV-S), respectively. Solid residues yielded 55.8% (MO) and 65.8 (MV) of the initial herb material subjected to HD. In total, 63 aroma compounds were identified and quantified in herbs by GC-TOFMS, accounting up to 88.4% of the total integrated GC area. Among 35 volatiles identified in MO EO the major compounds were geranial (24.7%), (*E*)-caryophyllene (11.6%), caryophyllene oxide (10.9%), neral (10.6%), citronellal (3.5%), 1-octen-3-ol (3.0%),  $\alpha$ -copaene/ $\alpha$ -humulene/ germacrene D (2.1%). In the HS of MO herb 45 volatiles were identified, however their percentage composition was different than in EO. For example, the content of 1,8-cineole in the MO HS and EO was 26.9% and 0.1%, respectively, that of (*Z*)-dihydro carvone 10.3% and 1.5%, respectively. The main volatiles identified in EO/HS of MV-L and MV-S were (*Z*)- $\beta$ -farnesene (38.9/38.8% and 32.1/19.4%), germacrene D (11.9/3.1% and 7.3/0.6%),  $\delta$ -cadinene (5.1/0.2% and 4.2/2.1%),  $\alpha$ -copaene (4.2/7.6% and 2.7/0.2%),  $\alpha$ -humulene (4.7/2.1% and 6.4/6.5%), respectively. High contents of limonene (8.4%) and menthone (8.3%) were found in the HS of MV-S, while in the EO these compounds were not detected.

The highest TPC was determined for WE of MO, 312.8 $\pm$ 1.5 mg GAE/g edw (WE<sub>S</sub>) and 307.7 $\pm$ 1.4 mg GAE/g edw (WE<sub>L</sub>). The TPC in MV WE varied from 21.4 $\pm$ 0.3 mg GAE/g edw (MV-S WE<sub>L</sub>) to 50.1 $\pm$ 4.7 mg GAE/g edw (MV-L WE<sub>S</sub>). WE obtained by spray drying resulted in slightly higher TPC content compared to lyophilized powder. The TPC in EOs was low, 2.5 $\pm$ 0.5 (MV-S) - 18.2 $\pm$ 0.6 (MV-L) mg GAE/g edw, because the main part of polar phenolics was dissolved in water during HD. The sum of TPC recovered with all plant processing fractions was from 9.1 $\pm$ 0.1 (MV-S) to 195.3 $\pm$ 0.9 (MO) mg GAE/g plant dw. This study revealed that lemon balm and white horehound herb are a good source of bioactive secondary metabolites, essential oil (volatile fraction) and phenolic (non volatile fraction) compounds, and could be used as natural flavourings and antioxidants in beverage and food industries.

## PECULIARITIES OF CATIONIC STARCHES SYNTHESIZED BY USING CaO

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Starch is biodegradable, renewable and relatively inexpensive biopolymer, which makes it attractive as an environmentally friendly material. Cationic starches are important commercial products, which are widely applied in different fields of industry, such as water treatment e.g. natural and waste water purification [1].

The aim of present investigation was to obtain cationic starches (CS) by cationization reaction with and without CaO as catalyst and to characterize obtained products by FT-IR spectroscopy, SEM, X-ray diffraction analysis as well as to evaluate their rheological properties.

Cationic starches of different degree of substitution (DS) were obtained by etherification of native potato starch with 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC) using NaOH and with and without addition of CaO (Fig.1). The highest DS of CS achieved by using CaO catalyst was 0.84 at the reaction yield of 84 %. Meanwhile, the DS of CS obtained without CaO catalyst was 0.28 at the reaction yield of 47 %.

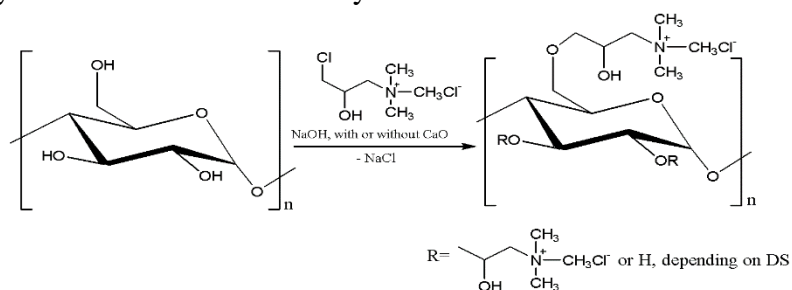


Fig 1. Starch cationization reaction using CHPTAC as cationization agent

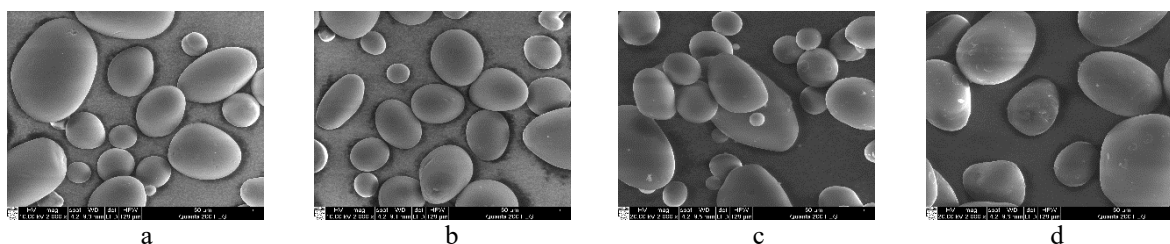


Fig. 2. SEM images of potato starch (a) and cationic starches synthesized without (b) and by using CaO as catalyst (c,d). DS of CS: b – 0.25; c– 0.25; d– 0.40. Magnification x 2000.

SEM images presented in Fig. 2 showed that the size of CS obtained without and by using CaO as catalyst is similar. However, the granules surface was more rough when CaO was used in the reaction. FT-IR spectra showed characteristic peaks of cationic starch. Furthermore, the rheological properties of CHPTAC modified starches by using CaO catalyst were very different from those obtained without CaO catalyst. The gelatinization of modified starches obtained by using CaO catalyst proceeded at similar temperatures compared to starches modified without the use CaO and viscosity of the final paste was significantly lower.

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## HYDROGEN GENERATION FROM NaBH<sub>4</sub> HYDROLYSIS USING CoBZn/Cu, CoBMo/Cu, CoBFe/Cu CATALYSTS

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Development of clean and sustainable energy sources is one of the main focus of scientific research. Hydrogen is considered to be eco-friendly energy source [1, 2, 3, 4]. Although hydrogen energy is very promising the wide application of is limited by finding effective hydrogen storage materials and efficient catalysts for hydrogen generation [3,5]. Sodium borohydride (NaBH<sub>4</sub>) is promising storage material due to stability in alkaline solutions, high theoretical hydrogen storage (10.8 wt%), stability at room temperature, low price, safe and efficient release of hydrogen and recyclability of reaction byproducts [2, 3, 4]. Hydrogen generation from sodium borohydride via hydrolysis reaction may be represented by the following equation ( $\Delta H = -300$  kJ/mol):



It is known that noble metals such as Pt, Ru, Pd, Rh are efficient catalyst for hydrolysis of sodium borohydride [3,5]. High price of noble metals is the main reasons why research for non-noble metal catalysts are very important. Many studies show that cobalt alloys are suitable catalyst for sodium borohydride hydrolysis due to large surface area and porous structure [1, 2].

In this study, CoBZn, CoBFe and CoBMo catalysts were prepared by electroless plating on copper surface when borane morpholine complex was used as a reducing agent. Field-emission scanning electron microscope (FESEM) and inductively coupled plasma – optical emission spectrometry (ICP-OES) was used to characterized cobalt catalysts surface morphology and elemental composition. The catalytic activity of prepared cobalt catalyst towards NaBH<sub>4</sub> hydrolysis reaction was determined by measuring the amount of generated pure hydrogen gas. Alkaline sodium borohydride hydrolysis was performed under different conditions It was determined that the highest hydrogen generation rate 53.5 kJ/mol was obtained using CoBMo/Cu catalysts when temperature was 343 K and the lowest generation rate 0.16 kJ/mol was obtained using CoBFe/Cu catalyst at the temperature 313 K. The lowest activation energy, 27 kJ/mol was received by using CoBMo/Cu catalyst.

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# MALONIC ACID ASSISTED REDUCTION OF GRAPHITE OXIDE: STRUCTURAL CHARACTERISATION

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Graphene is a thick sheet of  $sp^2$  hybridized carbon atoms. It has received broad interest in many areas of science and technology because of its unique physical, optical, chemical, mechanical and thermal properties. There are many approaches to graphene preparation, including mechanical exfoliation, epitaxial growth, carbon nanotubes cutting, chemical vapor deposition [1]. Chemical reduction of graphite oxide (GO) is recognized as the most promising method for large scale and rapid production at low cost. However, the most popular chemical reducing agents, such as hydrazine, hydroquinone, sodium borohydride, lithium aluminium hydride, are hazardous, toxic and corrosive. The product obtained using these reagents has poor electrical conductivity, due to the defects remaining in crystal lattice and have negative impact on bio-related applications, too [2,3].

In this work, we present the thermal reduction of GO in the presence of malonic acid (MA), which is a green and inexpensive reducer decomposing thermally at 135 °C. Graphite oxide was prepared from the natural graphite by the synthesis protocol reported by Yan et al. [4]. In a typical experiment, graphite powder was treated with conc.  $H_2SO_4$ ,  $K_2S_2O_8$  and  $P_2O_5$ . Later, this pre-oxidized graphite was subjected to oxidation by Hummers method using  $NaNO_3$ ,  $H_2SO_4$  and  $KMnO_4$  [5]. The obtained GO was reduced by adding malonic acid with ratio of 1:3 or 1:5 and thermal annealing under Ar gas atmosphere for 30 min at different temperatures 200 °C, 300 °C, 600 °C, 800 °C. Reduced GO products were analyzed by Fourier Transform infrared (FTIR) and X-ray diffraction (XRD) analysis. Furthermore, the thermal decomposition of GO, malonic acid and GO:MA (1:3) mixture was investigated by TGA/DSC.

The results show that the level of GO reduction to graphene phase depends on the reduction conditions. Reduction of GO at 200 °C and 300 °C results formation of an amorphous product. XRD analysis of products obtained at 600 °C and 800 °C shows a similar 'd' spacing of 0.350 nm with a hexagonal structure. It indicates the formation of a more ordered graphitic structure and reestablishment of  $sp^2$  network after annealing. Moreover, FTIR patterns of these samples exhibit a successful reduction of oxygen-containing groups (O–H, C=O, C–O–C, C–O).

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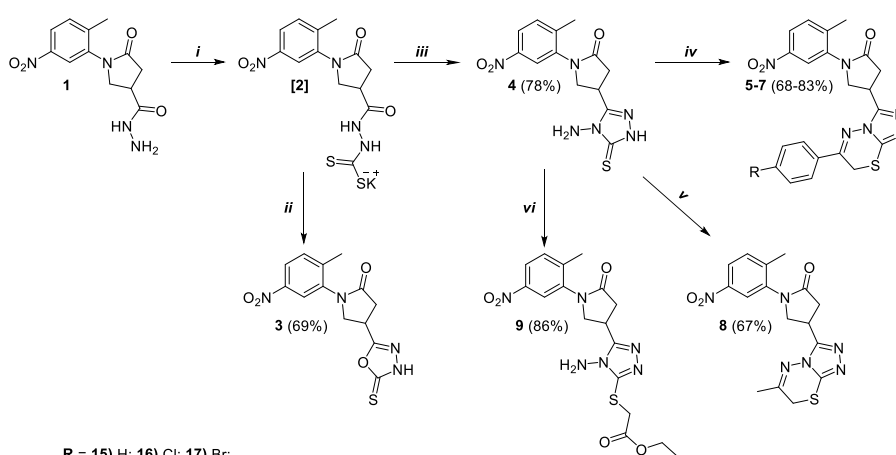
# SYNTHESIS OF NOVEL 1,3-DISUBSTITUTED 5-OXOPYRROLIDINES

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Azoles are particularly interesting for drug discovery since they have shown to possess a variety of biological activities including antimicrobial and antiviral [1, 2]. 1-(2-Methyl-5-nitrophenyl)-5-oxopyrrolidine-3-carbohydrazide (**1**) was used as a precursor for the synthesis of target nitrogen-containing heterocycles. 1,2,4-Oxadiazole derivative **3** was prepared by stirring a mixture of hydrazide **1**, CS<sub>2</sub>, and KOH in methanol at room temperature, followed by the dissolution of the resulting potassium dithiocarbazate **2** in water and treatment of the obtained solution with HCl to pH 6. Potassium dithiocarbazate **2** was also used for the synthesis of 4-amino-1,2,4-triazole derivative **4**, which was prepared by refluxing the aqueous solution of compound **2** with hydrazine hydrate and subsequent treatment of the obtained solution with acetic acid to pH 6. Potassium dithiocarbazate **2** was also used for the synthesis of 4-amino-1,2,4-triazole derivative **4**, which was prepared by refluxing the aqueous solution of compound **2** with hydrazine hydrate and subsequent treatment of the obtained solution with acetic acid to pH 6.



R = 15) H; 16) Cl; 17) Br;

i) CS<sub>2</sub>, KOH, methanol, rt, 24 h; ii) H<sub>2</sub>O, HCl, pH 6, rt; iii) N<sub>2</sub>H<sub>4</sub> · H<sub>2</sub>O, propan-2-ol, reflux, 72 h, glacial acetic acid; iv) 4-substituted 2-bromoacetophenone, 1,4-dioxane, reflux, 10 h, DMF, 10% CH<sub>3</sub>COONa<sub>(aq)</sub>; v) chloroacetone, 1,4-dioxane, reflux, 12 h, propan-2-ol, 10% CH<sub>3</sub>COONa<sub>(aq)</sub>; vi) ethyl chloroacetate, 1,4-dioxane, piperidine, rt, 10 h.

Triazolo[3,4-*b*]thiadiazine derivatives **5–8** were synthesized from 4-amino-1,2,4-triazole compound **4** by the condensation reaction with corresponding  $\alpha$ -haloketones. Since these reactions were carried out without a base, the data of elemental analysis showed that respective hydrobromic or hydrochloric salts of **5–8** were obtained. Reaction of compound **4** with ethyl chloroacetate and in the presence of piperidine at room temperature resulted in the formation of the only *S*-alkylated product **9**. Unfortunately, all attempts to cyclize compound **9** have failed. All of the synthesized compounds were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, IR and elemental analysis.

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## WAYS OF SULFUR WASTE RE-USE UNDER HYDROTHERMAL CONDITIONS

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270 million tons of sulfuric acid were produced during 2018 [1]. Consequently, large amounts of waste contaminated with sulfur element are generated in the production of sulfuric acid and its compounds [2]. In fact, one of the main fertilizer producers in Lithuania, a joint-stock company "Lifosa", generates approximately 550 tons per year of sulfur waste, which form during the filtration of molten sulfur. The waste consist of elemental sulfur, quartz and calcium compounds. Unfortunately, the mentioned waste is stored in landfill sites and can cause many environmental problems such as pH changes in a soil, acidic rains and other [2].

The sulfur waste was milled and mixed with water. The hydrothermal treatment has been carried out in stirred suspensions in autoclave, under saturated steam pressure for 0.5 h at various temperatures and different water and solid ratios. Rapid cooling procedure was performed after every experiment. The sulfur waste and obtained products were examined by XRD, XRF and STA analyses.

It was determined that sulfur waste can be purified to elemental sulfur by performing rapid cooling procedure after hydrothermal treatment. Impurities such as quartz and calcium compounds were separated due to particles sizes differences of the produced material. Most efficient conditions of purification were determined.

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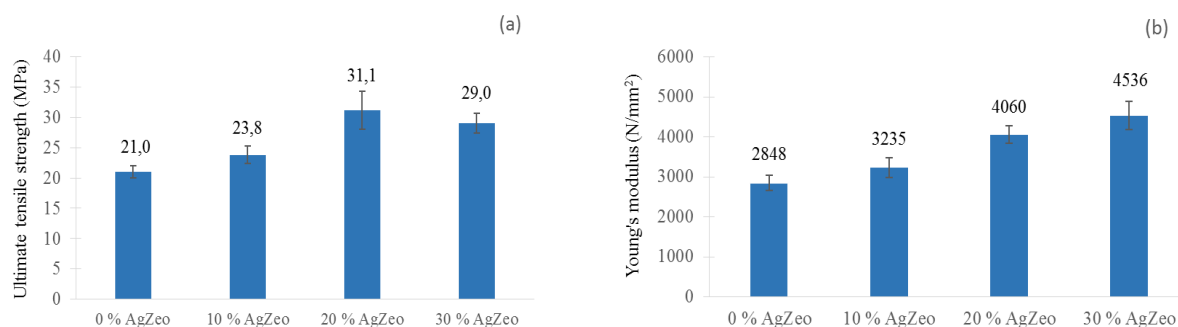
# THERMOPLASTIC CA/AgZeo COMPOSITE FILMS WITH ANTIMICROBIAL PROPERTIES

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Plastic waste has a negative impact on the environment and its pollution causes serious ecological problems [1]. Alternatively, biodegradable plastics are being developed to reduce environmental damage, with a shorter decomposition time than normal plastic. Nowadays, universality becomes the core value of the material world, therefore plastics are made with additives which are the essential elements of plastic properties, performance and long-term modification [2]. The inclusion of special properties, such as antimicrobial property in plastic, is an extension of its scope [3]. This applies to food, textile, medicine, pharmacy and other branches of industry [4]. The aim of this research is to determine the effect of silver zeolite (AgZeo) particles on the mechanical, thermal, optical, antimicrobial and biodegradation properties of plasticized cellulose acetate films. Mechanical characteristics are presented in figure 1.



**Fig. 1.** Mechanical characteristics of plasticized cellulose acetate films containing silver zeolite: ultimate tensile strength (a) and Young's modulus (b)

By increasing the amount of AgZeo additive in plasticized cellulose acetate films up to 20 wt%, ultimate tensile strength and Young's modulus films increases from 21.0 MPa to 31.1 MPa and from 2848 MPa to 4060 MPa, respectively, compared to plasticized cellulose acetate films. With the addition of 30 wt% of silver zeolite, Young's modulus further increases up to 4536 MPa, however, no further increase in ultimate tensile strength was observed, - value decreased to 29.0 MPa in that case. Therefore, the conclusion can be made, that 20 wt% concentration of silver zeolite in the aspect of mechanical properties provides optimum characteristics. In that case, silver zeolite not only provides antimicrobial properties, but also increases the tensile strength of plasticized cellulose acetate films.

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## AROMA PROFILE, TOTAL PHENOLICS AND ANTIMICROBIAL ACTIVITY OF SPEARMINT AND PEPPERMINT ESSENTIAL OILS AND WATER EXTRACTS

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Many aromatic herbs and spices, including spearmint (*Mentha spicata*) and peppermint (*Mentha×piperita*), are used as natural flavourings and a source of bioactive phytochemicals such as antioxidants and antimicrobials. The aim of the present study was to evaluate chemical composition and aroma constituents of spearmint (S) and peppermint (P) headspace and essential oil (EO), to determine the total phenolic content (TPC) and antimicrobial activity of EOs and water extracts (WE). Headspace of volatile compounds was analysed by solid phase microextraction and gas chromatography with time-of-flight mass spectrometry detector (HS-SPME-GC-TOFMS). The EOs were isolated in a *Clevenger* apparatus and analysed by GC-TOFMS. TPC was determined by Folin–Ciocalteu method and expressed in gallic acid equivalents in extract dry weight (mg GAE/g edw). The antimicrobial activity of oils against six foodborne pathogenic bacteria strains was analysed by the agar disk diffusion method, which measures inhibition zones (mm) in the plate count agar.

S/P herbs contained 11.8/12.6% moisture, 7.1/6.7% ash, 2.2/2.1% lipids and 19.0/48.2 mg/100g ascorbic acid. The yield of S and P EOs was 1.7% and 2.7%, respectively. The residues after distillation were separated into liquid and solid fractions by filtration. The liquid fractions were lyophilized and spray dried into WE<sub>L</sub> and WE<sub>S</sub>, yielding 31.1/20.9% (S) and 34.2/16.1% (P), respectively. The yields of solid residues were 59.7% (S) and 51.1% (P).

In total, 98 compounds were identified and quantified in the HS and EO of analysed herbs. Forty-five compounds accounting 99.6% of the total GC-peak area were identified in S-EO with major components (*Z*)-, (*E*)- dihydro carvones (61.8, 11.8%), linalool (8.5%), limonene (1.7%) and 1,8-cineole (4.8%). The percentages of more volatile monoterpenes in most cases were higher in HS, while oxygenated monoterpenes were dominant in EO. It may be explained by the higher vapour pressure of low molecular mass compounds. Linalool (28.2%), (*Z*)-dihydro carvone (18.6%), linalyl formate (18.1%), 1,8-cineole (8.5%), limonene (5.9%) and 3-octyl acetate (4.4%) were dominant compounds in S-HS. Forty-eight and 62 compounds were identified in P-EO and P-HS, respectively. The main volatile compounds in P-EO/HS were menthone (33.0/14.7%), *neo*-menthol (8.0/11.9%), menthol (24.3/18.7%), pulegone (13.4/18.2%), menthyl acetate (8.4/2.6%) and 1,8-cineole (4.0/1.6%).

The TPC values measured for EOs were low, from 2.9±0.2 (P) to 5.5±0.2 (S) mg GAE/g edw, because the majority of compounds reacting with Folin-Ciocalteu reagent are non-volatile polar antioxidants. Therefore, TPC in WE<sub>L</sub> and WE<sub>S</sub> was comparatively high, from 213.3±0.3 (S) to 238.1±1.2 (P) mg GAE/g edw and from 214.6±1.1 (S) to 253.8±1.2 (P) mg GAE/g edw, respectively. The sum of TPC recovered with all plant processing fractions was from 111.2±0.3 (S) to 122.6±0.6 (P) mg GAE/g plant dw. Antimicrobial effects of P-EO was in the following order: *B. cereus* > *E. coli* > *S. aureus* > *L. monocytogenes*; that of S-EO: *B. cereus* > *L. monocytogenes* > *S. aureus* > *P. aeruginosa* > *E. coli*. *S. enteritidis* was resistant against both essential oils, *P. aeruginosa* was stable against P-EO.

This study revealed that spearmint and peppermint herbs are a good source of bioactive secondary metabolites, volatile essential oil and non-volatile phenolic compounds, and could be used as natural antioxidants, antimicrobials and flavourings in food and beverage industries.

# HYDROGEL AND ENZYMES COMBINATION FOR PAPER DOCUMENTS CLEANING

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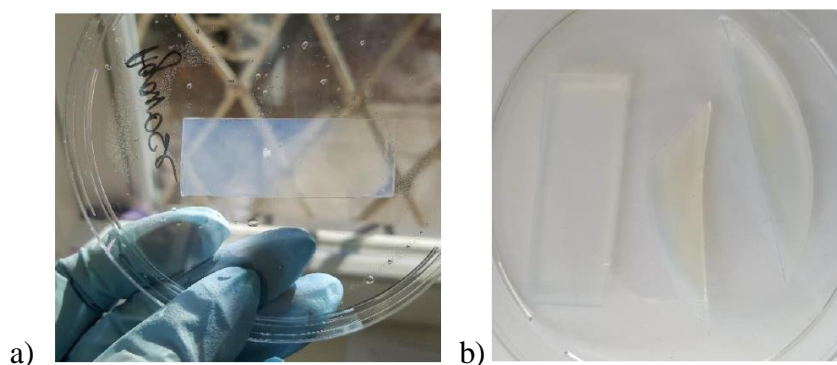
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Hydrophilic gels (hydrogels) are liquid-solid systems of a solid water-based matrixes that are able to swell but do not dissolve in water forming a three-dimensional network. The network consists of hydrophilic polymers that are swollen in water or inorganic additives that increase viscosity and retention. The properties of the hydrophilic material depend on the gelling agent, i.e. polymer functional groups (hydroxyl (-OH), carboxyl (-COOH), amide (-CONH-) and others) [1]. Also, these hydrogels could be used with other materials to improve their efficiency. Recently, hydrogels have been modified with various organic solvents, enzymes, neutralizing agents, biocides, etc. to improve and increase their capacity and selectivity for various cleaning procedures [2].

Given the importance of the preservation of paper medium, the objective of this study is to adapt the hydrogels and hydrolytic enzyme combination for paper cleaning process and to investigate their effect on paper properties. During this study the change of acid and optical properties of the paper samples, which were affected by hydrogels (TopVision Agarose, Gellan Gum Kelcogel CG-LA, Phytigel<sup>TM</sup>) and hydrolytic enzymes was examined. Paper samples were cleaned with hydrogels-enzyme composition, after samples were dried at room temperature. During research the following methods were used: SEM, FT-IR spectroscopy, colourimetry and acidity measurements.



1. Fig. Photo of TopVision Agarose gel a) before cleaning, b) after cleaning of paper sample.

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## APPROACH TO GREENER PROCESS: ENZYMATIC PICKLING OF HIDE

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Leather industry involves multiple operations before final product can be used as raw material. The use of chemicals in different leather processes such as lime, sulphide, chrome cause almost 80-90% of the pollution [1].

Due to growing interest in more environment friendly processes, leather industry started to use the concept of cleaner production to minimize their impact and reduce the loss of chemical, water and raw materials. Enzymes are gaining more recognition because of advancements made in purification, development and improvement, also they are considered as environmentally friendly [2]. Currently, enzymes are applied at various stages of leather processing like soaking, unhairing, bating, degreasing. However, more research is needed to study enzyme effect and application in leather industry.

The present study was devoted for evaluation of the enzymes impact during pickling and further processes. During the study, process was performed adding different enzymes preparations (EP) Lithudac L (FGL International, Italy) and Zime SB (River Chimica, Italy) into pickling solution (Sample I – Lithudac L 2%, Sample II – Lithudac L 0,5%, Sample III – Zime SB 3%, Sample IV – Zime SB 1%) and compared to control (Sample V). Both EP are proteases having activity in acidic medium. Pickling conditions (% from pelt mass): H<sub>2</sub>O – 80%, NaCl – 6%, HCOONa – 1%, H<sub>2</sub>SO<sub>4</sub> – 1.5%; temperature – 20°C; duration – 7 h.

Process efficiency was assessed determining amount of collagenous proteins in pickling solution, porosity and shrinkage temperature of hide, exhaustion of chrome compounds and their content in chromed samples. The results are presented in Table.

**Table.** Qualitative indexes of enzymatic pickling and chroming processes

Sample	Indexes of hide after process						
	Pickling			Chroming			
	Shrinkage temperature, °C	Porosity, %	Amount of removed collagenous proteins, g/kg of hide	Shrinkage temperature, °C	Porosity, %	Chromium consumption, %	Cr <sub>2</sub> O <sub>3</sub> in hide, %
I	55	55.6	0.52	94.0	55.9	57.9	2.60
II	48	60.9	0.27	95.2	58.2	47.4	2.50
III	59	59.8	0.35	104.5	55.6	58.0	2.65
IV	46	65.7	0.18	102.0	62.7	50.4	2.52
V	48	67.0	0.16	92.7	73.7	36.1	2.49

The obtained results show that EP used for pickling have considerable effect on collagen of hide during the process. The significant increase of the amount of removed collagenous proteins and the decrease of shrinkage temperature and of porosity of hide approve this proposition. The gained structural differences remain during the subsequent chroming and influences on the properties of chromed leather.

Research work is in progress.

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# BIPOLAR PHENOXAZINE-BASED COMPOUNDS AS NEW HOST MATERIALS FOR GREEN PHOSPHORESCENT OLEDs

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In the phosphorescent devices, to reduce quenching, triplet emitters are normally used as emitting guests in a host material, and thus suitable hosts are widely investigated for the phosphorescent devices [1, 2]. It is important that the triplet level of the host would be larger than that of the triplet emitter to prevent reverse energy transfer from the guest back to the host [3]. Another essential requirement is the ability of the material to form stable amorphous films [4].

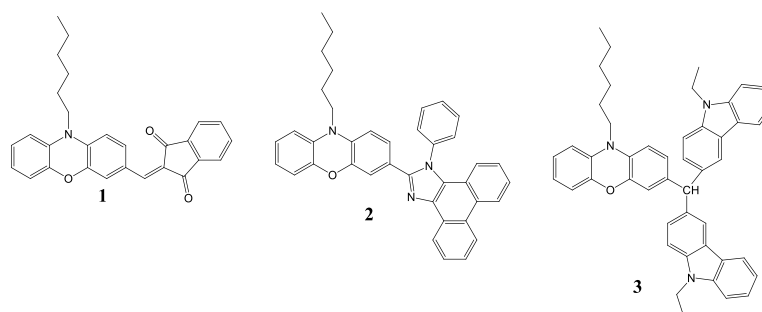


Fig. 1. Phenoxazine - based host materials

We report on the synthesis and characterization of a new series of bipolar phenoxazine-based compounds, shown in Fig. 1. Materials **2** and **3** formed homogeneous solid amorphous films with glass transition temperatures of 75 -93 °C. Layers of the synthesized compounds showed ionization potentials of 5.24-5.56 eV. Compounds **2** and **3** were tested as host materials for green phosphorescent OLEDs by using green triplet emitter of bis[2-(2-pyridinyl-N)phenyl-C](acetylacetonato)iridium(III) as the guests. The device with the host of material **3** exhibited the best overall performance. The efficient green OLED using the host demonstrated low turn-on voltage of 3.1 V, a maximum brightness of 5366 cd/m<sup>2</sup>, and maximum current efficiency of 18.3 cd/A. For the technically important brightness of 1000 cd/m<sup>2</sup> an efficiency above 15.7 cd/A was detected in the device.

**Acknowledgements.** The OLED materials were developed in the frame of project funded by a grant No. S-MIP-17-64 from the Research Council of Lithuania.

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# IMMUNOSENSOR FOR HUMAN GROWTH HORMONE DETECTION BASED ON INDIUM TIN OXIDE ELECTRODE WITH GOLD NANOSTRUCTURES

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Immunosensors are a type of biosensors based on immobilized antibodies (or antigens) and a signal transducer that converts the affinity interaction with the analyte to a signal that is proportional to analyte concentration [1]. Electrochemical signal transducers possess many advantages over optical and piezoelectric signal transducers such as the ease of miniaturization and versatility – a change in current, voltage or resistance can be measured [2]. Scientific and industrial impact of nanoscience and nanotechnology in analytical chemistry, medicine and pharmacy has been growing in recent years. In this field, gold nanostructures are the most widely used nanostructures due to their unique physical and optical properties [3]. Application of nanotechnology for immunosensor design results in higher stability of the sensors and increased analytical signal [4]. Human growth hormone (hGH) also known as somatotropin is essential for normal human development, therefore, a reliable quantitative detection of hGH is crucial [5].

The main aim of this study was to explore an immunosensor for human growth hormone detection based on indium tin oxide (ITO) coated glass electrode with electrochemically deposited gold nanostructures and covalently coupled antibodies against human growth hormone (anti-hGH). Nanostructured ITO electrode was characterized using scanning electron microscopy, X-ray diffraction and various electrochemical methods. Furthermore, anti-hGH were covalently coupled onto gold nanostructures using the self-assembled monolayer. The immunosensor based on this design was investigated for the direct detection of hGH using square wave, differential pulse and cyclic voltammetry methods.

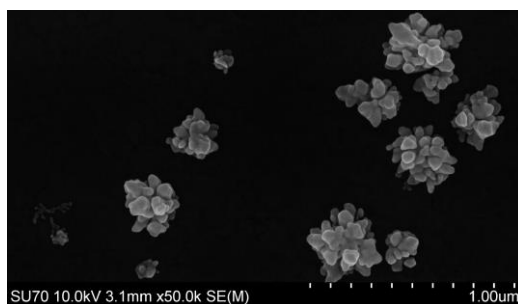


Fig. 1. Scanning electron microscope image of gold nanostructures on ITO coated glass electrode.

## Acknowledgments

This research is/was funded by the European Social Fund under the No 09.3.3.-LMT-K-712-10-0168 “Development of Competences of Scientists, other Researchers and Students through Practical Research Activities” measure.

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# HOLE-TRANSPORTING MATERIALS FOR PEROVSKYTE SOLAR CELLS CONTAINING TRÖGER'S BASE CORE AND ENAMINE-LINKED DIPHENYL MOIETIES

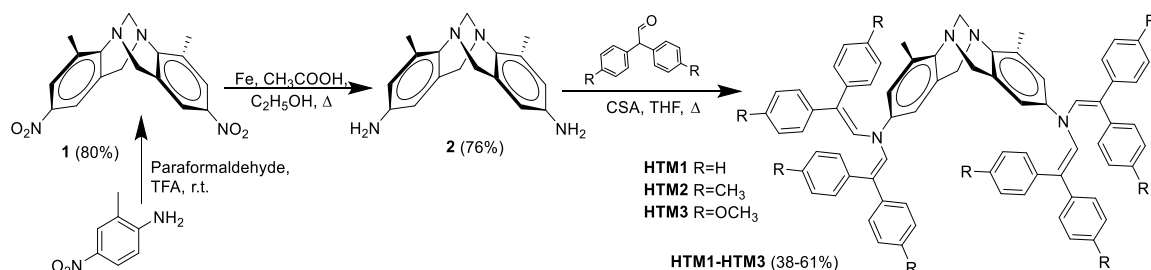
Titas Braukyla,<sup>[a]</sup> Rui Xia,<sup>[b]</sup> Marytė Daškevičienė,<sup>[a]</sup> Tadas Malinauskas,<sup>[a]</sup> Alytis Gruodis,<sup>[c]</sup> Vyngintas Jankauskas,<sup>[c]</sup> Cristina Roldán-Carmona,<sup>[b]</sup> Cristina Momblona,<sup>[b]</sup> Vytautas Getautis,<sup>\*[a]</sup> Mohammad Khaja Nazeeruddin<sup>\*[b]</sup>

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Perovskite solar cells (PSCs) are a promising affordable alternative to inorganic solar cells for efficient harvesting of abundant solar energy with high power conversion efficiency. Until now, most of the high efficiency PSCs are based on either small organic molecule 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxy-phenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) or conjugated macromolecule poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) hole-transporting materials (HTMs), both of which are expensive due to expensive multi-step synthesis and costly purification procedures [1], [2]. As HTMs are essential part in solar cell manufacturing, currently they are a bottleneck for the realization of cost-effective and stable devices. Tröger's base (TB) is an easily obtainable angle-shaped molecule and can serve as a structural core, providing non-planar orientation for its substituents and structural branches towards each other. Expanding TB structure *via* enamine condensation can increase both structural bulk and expand conjugated  $\pi$  system multiple times, thus providing easily obtainable, cheap and efficient HTMs for PSC applications.



**Scheme 1.** Synthesis of Tröger's base compounds **HTM1–HTM3**

Here we report the synthesis of three novel enamine HTMs based on Tröger's base scaffold. These compounds are obtained in easy three-step synthesis from commercially available materials, none of the synthetic steps requiring expensive palladium catalysts or inert conditions. Two best performing HTMs are purified via crystallization, hence eliminating the need of column chromatography. Best performing material **HTM3** demonstrated 18.62 % PCE in PSC, rivaling Spiro-MeOTAD in efficiency, and also showed superior stability of non-encapsulated perovskite cell; while tested in dopant-free PSCs it outperformed Spiro-MeOTAD by 1.6 times. High glass transition temperature ( $T_g = 176$  °C) of **HTM3** also hints its bright perspectives in device applications.

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## VAPORIZATION OF ADIPATE PLASTICIZER FROM POLYISOPRENE FILMS

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Technical performance and service life of rubber is strongly affected by plasticizer migration. A new test method was developed to evaluate volatile emissions of plasticizers in a polymer matrix based on thin film degradation test [1]. Test specimens were prepared from di-2-ethylhexyl adipate (Aldrich, Germany) and polyisoprene SKI-3S (UAB MLCH, Lithuania) with Mooney viscosity between 61 to 71 and tensile strength of 21.6 MPa at 100°C, drying loss of 1.2%, antioxidants 0.7% to 1.9%, ash content of 0.35% and stearic acid 0.5% to 1.5%. They were blended on a two roll mill HTR-300 (Hartek Technology Co, China) at 30°C to 40°C, 10-15 m/min velocity and 1.18 slide ratio. The polymer was pre-plasticized and each specimen was prepared by obtaining a continuously cycling rubber band of 20 to 50 g initially. Then the roll gap was gradually narrowed down to 0.1 mm and the specimen cycled for over 20 passes. The band was weighed and 2EH adipate was added by dropping a small amount onto the band center and folding it to avoid leakage before cycling it again. Plasticizer addition and specimen cycling were repeated until the needed weight was achieved.

Flat sides of cylindrical metal coupons of 16-19 mm in diameter were polished, degreased, dried, weighed and coated with specimen chunks, which would eventually creep into a continuous film of 500 µm thickness, as calculated from the coated area. The coupons were placed into an oven (Memmert, Germany) at 120°C or 140°C and periodically removed for weighing to measure the volatile losses, as plotted in Fig. 1.

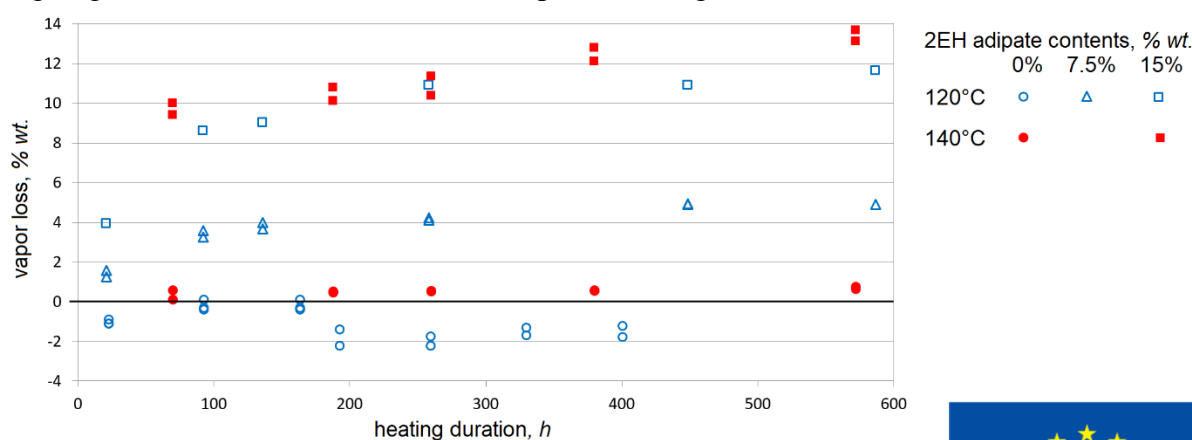


Fig. 1 Volatile emissions from p-isoprene films with and w/o 2EH adipate plasticizer.

The results show good repeatability, demonstrating that larger concentrations of 2EH adipate lead to higher emissions. However, despite long heating durations, not all plasticizer was lost, which suggests that some of it is strongly bound in the polyisoprene matrix. The test makes it possible to compare plasticizer migration trends of different esters, polymers, additives and compounding procedures.

### Acknowledgment

The project COSMOS has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 645405.

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**COSMOS**  
ADDING VALUE TO CAMELINA AND CRAMBE OIL

## XRD STUDY OF THIN SnS FILMS ON FTO GLASS

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In recent years tin sulfide (SnS) has been gaining more and more attention due to its potential as a solar cell photo-absorption layer [1]. Theoretical-experimental studies showed that this material has an indirect bandgap ( $E_g$ ) of 1.049-1.076 eV and a direct bandgap of 1.296 eV [2]. Also SnS has a high absorption coefficient that it exhibits in this thin film state [1].

Thin SnS films can be gained using a lot of different techniques, such as vacuum evaporation, chemical bath deposition, spray pyrolysis and etc [3]. Based on all these studies now are known, that tin sulfide in crystalline state is a layered chalcogenide compound with strong anisotropic behavior [1]. In this work SnS layered structure was gained by using SILAR technique.

SnS thin films were prepared on FTO glass. The ultra-sonic cleaning of glass slides was carried out by dipping the glass slide into acetone at 40 °C for 10min, then rinsed with distilled water and dried. As the cationic precursor were used 40 °C 0.1M SnCl<sub>2</sub> solution and as the anionic precursor – 40 °C 0.1 M Na<sub>2</sub>S. Sample No 1 was prepared by 3 steps: firstly precleaned glass substrate immersed in the cationic precursor for 30 s, then in the anionic precursor for 30 s and then in distilled water for 20 s. Sample No 2 was prepared by 2 steps: precleaned glass substrate immersed in cationic precursor for 30 s and then in the anionic precursor for 30 s. The precleaned substrate firstly immersed in the cationic precursor and tin ions were adsorbed on the surface of the substrate [4]. When the glass slide immersed in the anionic precursor solution, sulfide ions reacted with tin ions which were adsorbed on the substrate. Twenty such deposition cycles were repeated in order to get adherent film. For both samples the last step was immersing these in the cationic precursor for 30 s. XRD technique was carried out by using a Bruker AXS D8 Advance diffractometer.

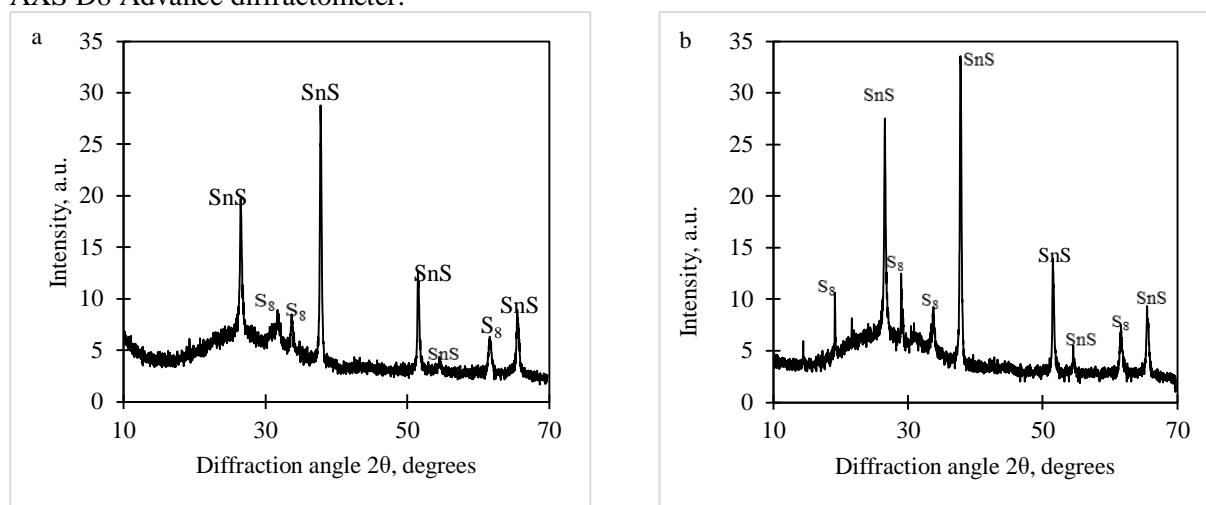


Fig. 1. a – sample No 1, b – sample No 2.

The phase composition of the formed films was resolved by contrasting their X-ray diffraction pattern with those of known minerals. In these films are SnS (83-47), S<sub>8</sub> (74-1465) peaks. The most intensive peak in both diffractograms are at  $2\theta=37.84^\circ$  and assigned to SnS. When the layer are formed without distilled water (Fig. 1 b), peaks of tin sulfide are more intensive than by using of water (Fig. 1 a).

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# DIGITAL IMAGE CHARACTERIZATION OF ELECTROCHROMIC CONDUCTING POLYMER AND TEXTILE COMPOSITES

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Color is one of the most important parameters we use to evaluate our surroundings. While understanding color signals correctly is crucial in our everyday life, it also has a lot of sentimental meaning. Color, or change in color can be used to express emotions or just for aesthetic reasons. A promising way to create flexible communicative devices is combining electrochromic materials with textile substrates. Electrochromic conductive polymers provide a great variety of colors [1], rapid response times and are comparatively easy to work with [2].

In this study, we report the electrochemical synthesis and characterization of conducting polymers polyaniline (PANI) and 3,4-dioxythiophene (PEDOT) and textile substrate composites. Potential induced electrochromic color change of conductive polymer composites was filmed and then analyzed with video analysis software ImageJ. All videos were taken in special recording box with LED lighting. Using ImageJ every pixel is expressed as combination of three primal colors: red (R), green (G), blue (B) [3]. During the analysis color channels are separated and the change of their intensities in time measured (Fig. 1).

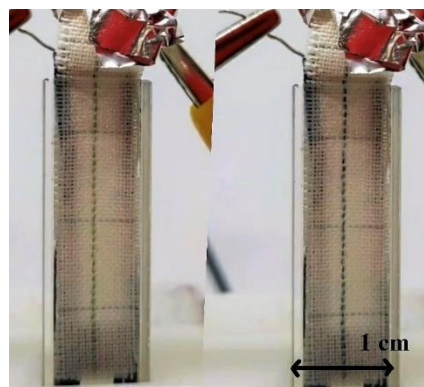
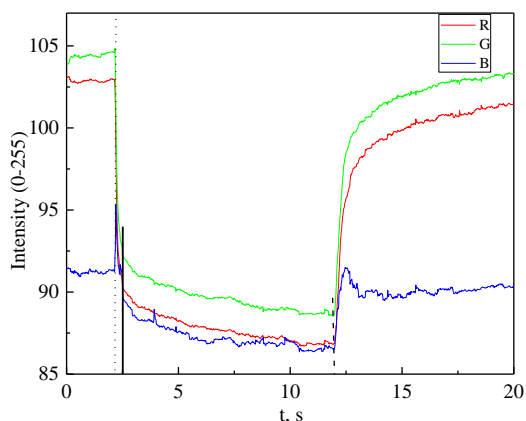


Fig. 1 Color intensity measurement of PANI-PES-Cu-Ni Fig. 2 Electrochromic color change of polyaniline

Conductive polymer and textile structures demonstrated reversible color change that was successfully evaluated using ImageJ. Visible color for PEDOT is from dark to light blue and for PANI from green to blue (Fig. 2). These results indicate that there is a great potential provided by textile and conductive polymer composites creating flexible wearable displays in the future.

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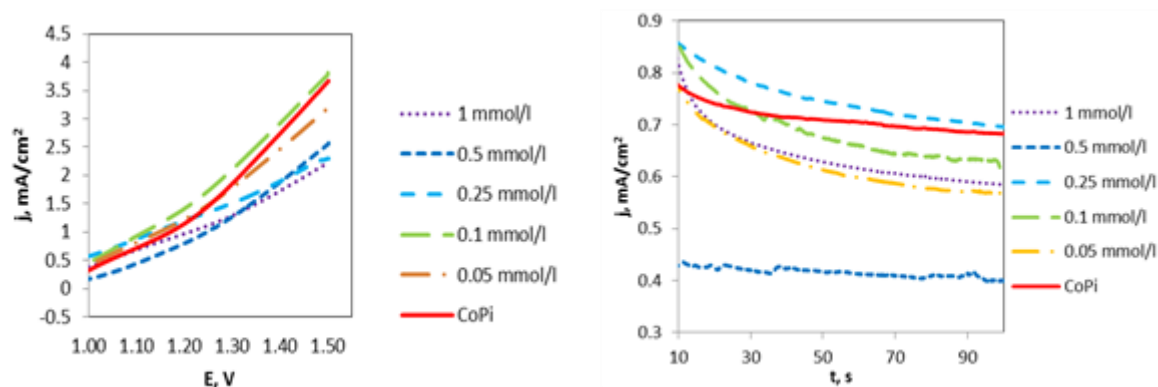
# ELECTROCHEMICAL DEPOSITION AND ELECTROCATALYTIC ACTIVITY OF Co-Ni PHOSPHATE COATINGS

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The hydrogen production by water electrolysis using renewable energy sources is a clean alternative to fossil fuels. The limiting step for the electrolytic splitting of water is the oxygen evolution reaction [1] and the most efficient catalysts for anodic oxygen evolution reaction are quite expensive. Due to these reasons, much attention is paid to the iron group metals, particularly to cobalt phosphate based electrocatalyst, which is effective at neutral pH values [2]. In the attempt to increase the activity of the Co-Pi (Pi - inorganic phosphate) electrocatalyst it is modified with various additives. The purpose of this work was to determine influence of Ni additive to the activity of modified Co-Pi electrocatalyst. The potentiostatic technique was used for deposition of amorphous Co-Pi and Co-Ni-Pi electrocatalyst coatings on the electrically conductive glass from an aqueous phosphate buffer solution (pH=7,0) containing 1,0 mmol/l  $\text{Co}(\text{NO}_3)_2$  and different concentrations (0,05-1,0 mmol/l) of  $\text{Ni}^{2+}$  ions additive. The electrolytic deposition lasted for 20 min. at 1,1 V potential.



**Fig. 1.** Results of linear sweep voltammetry (left) and chronoamperometry (right) tests of Co-Pi and Co-Ni-Pi coatings in aqueous 0,1 mol/l phosphate buffer (pH=7) solution. Coatings were obtained from neutral aqueous phosphate buffer solution containing 1,0 mmol/l  $\text{Co}(\text{NO}_3)_2$  and different concentrations of  $\text{Ni}^{2+}$  ions.

Linear sweep voltammetry conducted at 25 mV/s revealed that coatings with a small amount of Ni had a higher current density than a pure Co-Pi coating. An increase of current up to 23% was observed in the case of the coating which was deposited from the solution containing 0,1 mmol/l  $\text{Ni}^{2+}$  additive. In order to ascertain the long term effectiveness of the catalyst, a chronoamperometry tests lasted for 5 min at 1,2 V potential. It was observed that after the first minute the anodic current density for the modified Co-Ni-Pi catalysts coatings equalized to or became lesser than for the pure Co-Pi catalyst. Any perceptible increase in effectiveness of the modified catalyst over the standard one is only temporary and quickly disappears over prolonged electrolysis. In some cases, higher Ni amounts in the coating actually had a negative effect on the performance of the catalyst.

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# SURFACE PLASMON RESONANCE IMMUNOSENSORS FOR HGH DETECTION

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Human Growth Hormone (HGH) is a peptide hormone that is secreted by the anterior pituitary gland. HGH is responsible for tissue development, formation of bones and muscles and it is important not only for children but also for adults. The lack of hormone can increase a risk of developing health problems, such as poor memory, depression, reduced heart muscle function. Increased levels of HGH produces high blood pressure, sleep apnea. An excess of HGH can also be caused by pituitary tumors [1]. Therefore, it is important to maintain sufficient levels of HGH in the body. Since 1960 HGH produced by pituitary was used as an experimental treatment for children who suffered from lack of HGH. Side effects were registered only thirty years later. In 1981 Genentech developed the first recombinant HGH (rhHGH) by a biosynthetic process. Since then therapy using rhHGH is used in medicine for Turner syndrome, Prader-Willi syndrome, Noonan syndrome treatment [2]. Because normal levels of the HGH in blood serum are only 2.73 – 227.27 pmol/L, very sensitive analytical methods are required. A powerful tool for determination of the HGH concentration in complex samples can be surface plasmon resonance (SPR) immunosensors that detect interactions between immobilized biologically active substance and analyte in real-time and it is possible for multiple analysis, if proper regeneration conditions are presented [3]. Since the size of an analytical signal of the SPR immunosensor depends on the molecular weight of the substance to be determined, the sensitivity of the assay is dependent on a concentration determination method. Direct method can be used if molecular weight of analyte is more than 10 kDa. Indirect methods are more suitable to analyze small biomolecules and to detect low analyte concentrations. In this work two HGH SPR immunosensors were designed and compared. One of them was able to detect HGH in a direct method and the other in an indirect competitive inhibition method.

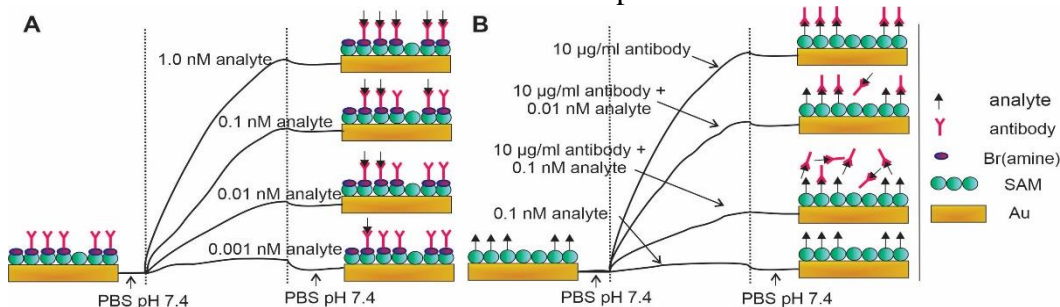


Illustration of analyte concentration determination: A – direct method, B – indirect competitive inhibition method. Br(amine) – 3- against HGH.aminophenylboronic acid; SAM – self-assembled monolayer; Au – gold coated SPR sensor chip; analyte – HGH; antibody – antibody

## Acknowledgements

This research is/was funded by the European Social Fund under the No 09.3.3- LMT-K-712 “Development of Competences of Scientists, other Researchers and Students through Practical Research Activities” measure.

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# SYNTHESIS AND ANTIMICROBIAL ACTIVITIES OF CARBAZOLE-BASED COMPOUNDS

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Even though there are many antibacterial agents multidrug resistant bacteria poses a huge threat to public health and has become one of the biggest health problems in the last decade. Therefore, there is an urgent need to develop novel and more potent antibacterial agents [1].

Carbazole is, a nitrogen containing aromatic heterocyclic compound, which can be found in nature as carbazole alkaloid that is isolated from various part of the plant. Such carbazole ring containing alkaloids are carbomycins. They showed good activity against various organisms, which made carbazoles a desirable target for further biological research [2]. Carbazole and its derivatives are extensively used in various chemistry fields such as photoelectrical materials, dyes, supramolecular recognition [3,4,5,6]. Therefore, carbazole and its derivatives are attractive target to develop and produce new antibacterial compounds.

In this work a series of carbazole-based derivatives were synthesized, and their antibacterial activity was evaluated against *Bacillus subtilis* and *Escherichia coli*. Various functional groups were introduced into carbazole-based compounds in order to investigate their biological activity. Synthesized compounds were screened for their *in vitro* antibacterial activity according to the disk diffusion method. The minimum inhibitory concentration (MIC) was determined by the serial dilution technique using dimethylsulphoxide (DMSO) as a solvent. All compounds were evaluated at the concentrations of the antibacterial agents ranging from to 31.25 to 1000 µg/mL and compared against ciprofloxacin and amoxicillin after overnight microorganisms growth. The results are displayed in Table 1.

**Table 1.** Antimicrobial activity data of carbazole-based compounds.

Compound	1a	1b	2a	2b	3	4	5	Amoxicillin	Ciprofloxacin	
MIC (mg ml <sup>-1</sup> )	<i>B. subtilis</i>	31,25	250,00	31,25	31,25	62,50	125,00	>1000	62,50	3,90
	<i>E. coli</i>	125,00	250,00	62,50	62,50	31,25	250,00	>1000	62,50	3,90

DMSO – negative control.

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# SYNTHESIS AND INVESTIGATION OF BIOCOMPATIBLE FILMS FROM POLY(VINYL ALCOHOL) MODIFIED WITH EPOXY COMPOUNDS

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Insufficient amount of organ donors results in the lack of organs for transplantation. In order to solve this problem, a lot of effort has been poured into the field of tissue engineering. The aim of this field is to create biological substitutes, that repair or even improve tissue functionality [1]. Poly(dimethylsiloxane) (PDMS) is one of the most commonly used silicone based polymers in the world, because of its great properties such as biocompatibility, gas permeability, thermal stability, transparency, and general cheapness of the polymer [2]. However, because PDMS is hydrophobic it has limited use in biomedicine, and needs to be modified. Poly(vinyl alcohol) (PVA) could be used for this purpose because of its hydrophilic tendencies, biocompatibility, and non-toxicity [3]. In the past, desirable characteristics were obtained by modifying PVA with epoxy compounds such as glycidyl methacrylate (GMA) through transesterification or epoxide ring-opening mechanisms [4].

The aim of this work was to modify PVA with diepoxy-PDMS (DE-PDMS) and/or monoepoxy-PDMS (ME-PDMS), GMA and 1,4-butanediol diglycidyl ether (BGDE). Films were obtained by curing of modified PVA via photopolymerization with photoinitiator IRG651. Glycerol was used as a plasticizer, to prevent films from becoming brittle. FT-IR and scanning electron microscopy (SEM) with high current mode for EDS was used in order to validate the structure of modified PVA. Swellability of films decreased when larger amounts of BGDE were used. When adding BMA before curing, films were the most swellable, while using GMA they were least swellable. Best Young's module (4,1 MPa) and relative elongation at break (36,1 %) compared to other films were observed when using initial component ratio [PVA]:[DE-PDMS]:[ME-PDMS]:[GMA]:[BGDE]= 1:0,1:0,1:0,2:0,1. Furthermore, using this film composition the largest Si content (15 %) was obtained. Generally stronger films were obtained using DE-PDMS, because of two epoxy rings, however the flexibility improved with the addition of ME-PDMS.

In order to see if films could be used in tissue engineering, biocompatibility tests were performed on rat myogenic cells and it was observed that our films had greater compatibility than commercial PDMS.

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# HIGHLY BIOBASED COMPOSITES FOR INJECTION MOULDING APPLICATIONS

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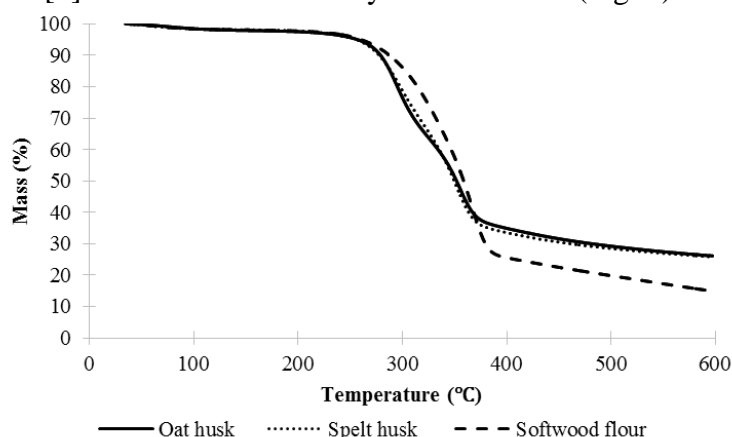
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Over recent decades, composite technology has come to rely heavily on petroleum-based resins and man-made fibers in the pursuit of more reliably and highly performing products. On the other hand, renewable raw materials offer advantages in terms of decreased dependence on fossil resources and reduced CO<sub>2</sub> foot print in accord with sustainability ideas and climate protection. Therefore, replacing petroleum-based raw materials with renewable resources is now a major concern in terms of economical and environmental viewpoints.

Lignocellulosic materials provide several advantages such as being lightweight, having a low density, low cost, high specific properties, low energy consumption generation of a rural/agricultural-based economy. Most widely known natural-organic fillers are wood flour. However, grain husks also contain a great amount of cellulose and hemicellulose which makes them similar to wood [1]. Their thermal stability is also similar (Fig.1.)



**Fig.1.** Thermogravimetric curves of different grain husks and softwood flour under N<sub>2</sub> environment

At the moment, grain husks produced from harvesting are mostly used as a fuel, producing energy through direct combustion. However, rather than burning, such agricultural waste can be used to produce higher-added value products [2]. Therefore, the aim of this works was to prepare polypropylene composites containing milled grain husks and to investigate their properties.

**Acknowledgement.** The authors are grateful to the Research Council of Lithuania for financial support of the project HyBiCo (S-M-ERA.NET-17-3).

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# DEVELOPMENT OF FLUORINATED BENZENESULFONAMIDES AS CARBONIC ANHYDRASE IX INHIBITORS

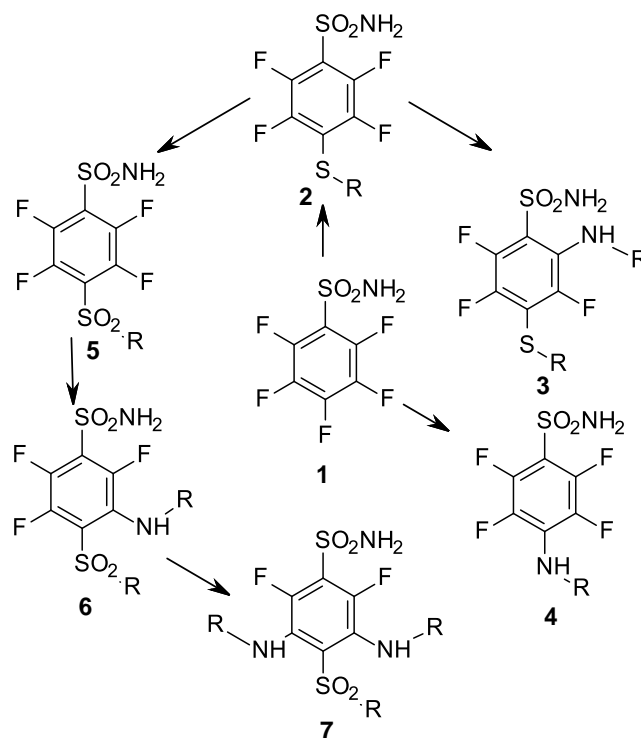
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Carbonic anhydrases (CA) are zinc metalloenzymes, which catalyze the reversible hydration of carbon dioxide and regulate a broad range of physiological functions. There are 12 active CA isoforms in human which differ in cellular localization, distribution in organs and tissues, expression levels and kinetic properties. The increased activity or expression of different CA isoforms is often associated with various diseases. Isoform CA IX is implicated in cancer since its expression is nearly absent in healthy human but overexpression of CA IX in numerous hypoxic tumors is observed. Design of a selective and high-affinity inhibitor could be developed into an anticancer drug.

Here we investigate fluorinated benzenesulfonamides as CA inhibitors. The fluorine atoms contributed favorably to CA binding. Furthermore, the fluorinated benzenesulfonamides were subject to convenient nucleophilic aromatic substitution reactions which enabled the synthesis of a diversity of fluorinated compounds. A series of 4-substituted-2,3,5,6-tetrafluorobenzenesulfonamides (**2**, **4**, **5**), 2,4-substituted-3,5,6-trifluorobenzenesulfonamides (**3**), 3,4-substituted-2,5,6-trifluorobenzenesulfonamides (**6**), and 3,4,5-substituted-2,6-difluorobenzenesulfonamides (**7**) were synthesized. Some of the fluorinated benzenesulfonamides bearing bulky hydrophobic groups at *ortho* and *meta* positions exhibited high selectivity and picomolar affinity for CA IX as confirmed by the binding assays. Crystallographic analysis showed the position of the compounds bound to CA IX and the effects in 2D and 3D cancer cell culture models of lead compounds showed compound anticancer activity.



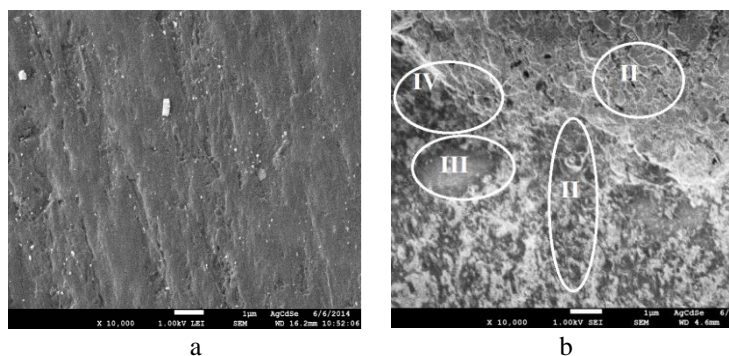
# MORPHOLOGY OF POLYAMIDE 6/Se-S-Cd-Ag COMPOSITE MATERIALS

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The concept of ion exchange reactions from pre-synthesized nanostructures can greatly expand the scope and diversify inorganic semiconductor nanomaterials as it provides reactive capabilities in tuneable composition and property solutions, while also extending the method application to a large scale [1]. Recently we have extended cation exchange reaction strategy to inorganic-organic hybrid materials synthesis [2] A cation-exchange reaction between  $\text{Cd}^{2+}$  and  $\text{Ag}^+$  was performed in an attempt to modify inorganic-organic PA-CdSe-CdS composite. XRD patterns showed a complex PA-Se-S-Cd-Ag film crystalline composition with hexagonal CdSe (JCPDS#77-2307), monoclinic  $\text{Ag}_2\text{S}$  (JCPDS#75-1061) and orthorhombic  $\text{Ag}_2\text{Se}$  (JCPDS#75-1061) peaks. Indeed, before applying such relatively new materials on functional devices, it is essential to provide a study of its properties. The aim of this study was to investigate PA-Se-S-Cd-Ag composites properties, in particular regarding their morphological characterization. Scanning electron microscope images acquired using a Phillips FEI XL30 FEG-ESEM and FEI Sirion HR-SEM using accelerating voltage of 1 kV, magnification  $\times 100000$ . No sample preparation – coating – before imaging performed.



**Fig.** SEM images of PA-Se-S-Cd (a) and PA-Se-S-Cd-Ag (b) composite materials.

The surface of starting PA-Se-S-Cd (Fig. a) material displayed faced surface including large-area dense and uniform blocs and different sized voids. After cation-exchange with  $\text{Ag}^+$  in aqueous solution the surface morphology of starting material transfer to complex architecture demonstrating the intrinsic property of the cation exchanger. The SEM image (Fig. b) shows a highly inhomogeneous surface architecture composed of flat lamellar regions (marked as I), complicated clumps (marked as II) deep voids with sharp boundaries (marked as III) and grid-like structures (marked as IV). The negative chemical formation energies of CdS and  $\text{Ag}_2\text{S}$  favour the creation of Cd-S-Ag interfacial bonds leading to nonselective nucleation in  $\text{Ag}_2\text{S}/\text{CdS}$  heterostructures [3]. It seems that at initial short exposure time of PA-CdSe-CdS in  $\text{AgNO}_3$  solution exchange of  $\text{Cd}^{2+}$  ions from CdS lattice leads to the formation of  $\text{Ag}_2\text{S}$  nuclei's on the top surface of starting material. As the  $\text{Ag}^+$  exchange progresses, these  $\text{Ag}_2\text{S}$  particles begin to grow causing the formation of complex surface morphology.

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## AQUEOUS SOL-GEL METHOD

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Fuel cells efficiently convert chemical energy to electricity in a silent and environmentally friendly way. Among the various kinds of fuel cells, solid-oxide fuel cells (SOFCs) have the advantages of the highest energy conversion efficiency and excellent fuel flexibility because of their high operating temperature. The high working temperature necessary to make oxide ions mobile enough in the electrolyte (e.g. 1273K for stabilized zirconias). Such a high operating temperature is beneficial for improving the electrode reaction kinetics and reducing the electrolyte ohmic drop [1]. Such conditions have some drawbacks like as seal in high temperature, interface reaction between components of SOFC, the sintering of the electrodes and more [2]. This operating temperature could be lowered by reducing the current electrolytes thickness or by finding more efficient electrolytes [3]. Recently, the new family of fast-oxide ion conductors whose parent compound is  $\text{La}_2\text{Mo}_2\text{O}_9$  was discovered. This material high conductivity is associated with a phase transition from the room-temperature monoclinic  $\alpha$ -form to a high-temperature cubic  $\beta$ -form at 853K while increasing oxygen ion conductivity of almost two orders of magnitude [4]. On purpose, to stabilize cubic phase at room temperature, lanthanum molybdate could be doped by different elements in the La, Mo, and O sites. It was observed that La site substitution with lower valence cations such as  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$  and another could stabilize cubic phase and increase oxygen-vacancy concentration [5, 6]. Moreover, oxygen ion transport properties strongly depends on preparation methods. To eliminate impurities, porosity and other drawbacks it is important to choose the right synthesis method, starting materials and reaction conditions, which could influence these disadvantages. In this paper, the aqueous sol-gel synthesis was successfully used to synthesize lanthanum molybdate doped by calcium with the initial composition of  $\text{La}_{1.9}\text{Ca}_{0.1}\text{Mo}_2\text{O}_{8.95}$ . Tartaric acid and citric acid was used as chelating agents. The synthesized gel precursors were heat-treated at 1273K for 5 h. The obtained powders were additionally pelletized and sintered in air at 1473 K for 5 h. To investigate thermal decomposition and possible mechanism of synthesised ceramics thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) were carried out. For crystal structure determination X-ray diffraction (XRD) analysis was performed. Moreover, the influence to the resulting surface morphology of different chelating agent, starting materials and amount of dopant was investigated using the scanning electron microscopy (SEM).

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# UV-CURED FILMS FROM POLYESTERS MODIFIED WITH $\alpha,\omega$ -DIHYDROXY-POLY(DIMETHYLSILOXANE)

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Tissue engineering is rapidly developing field that aims at creating functional constructs that mimic the properties of the extracellular matrix of the native tissues. It has become a promising approach to cure a number of diseases, damaged tissues or organs [1]. The tissues are grown on a synthetic artificial carcass which is created using UV-curing. It is very important to choose the right materials for the frame, it must be biocompatible, so that the cells could reproduce and functionalize, it must have mechanical strength, be flexible, biodegradable, easy to process and non-toxic [2]. Poly(dimethylsiloxane) (PDMS) elastomer is one of those biocompatible polymers due to its properties such as: non-toxicity, biocompatibility, gas permeability, thermal stability, chemical and biological inertness. However, its use is limited by hydrophobicity which can cause cellular adhesion on the surface to be short-lived, abrasion in the body and low mechanical resistance. PDMS could be modified to improve hydrophilicity, and then the ability to use PDMS significantly enhanced [3]. One of the possible modification methods is polyesters modification by hydroxyl terminated PDMS.

Polyester films were synthesized from azelaic acid (AA), maleic anhydride (MA), diethylene glycol and were chemically modified with hydroxyl terminated PDMS, at various initial molar ratios. Glycidyl methacrylate (GMA), buthyl methacrylate (BMA) and/or 2-hydroxyethyl methacrylate (HEMA) were used as curing agents to obtain UV-curable films. Resins were cured by free-radical polymerization using initiator Irgacure 651 and UV light. Chemical structure of films was investigated by FTIR,  $H^1$  NMR and EDS. The films were tested for swelling degree and solubility in hexane, ethanol and water. Films with higher concentration of azelaic acid were less soluble in hexane, that's means that PDMS incorporation in polymer was better when azelaic acid concentration was higher. The films were less soluble in ethanol when amount of maleic anhydride was higher, because there is larger number of double bonds in the polyester chain. The films with higher amount of maleic anhydride swelled less in ethanol. High film swelling degree in both ethanol and water was obtained when HEMA was used for UV curing because of it is able to absorb large amounts of water due to the hydrophilic group. The amount of Si in cured films varied in the range from 0,6 % to 8,3 % and was higher when films were synthesized with higher amount of azelaic acid. Obtained films exhibit good wettability in comparison to commercial PDMS film (Sylgard 184), their water contact angle was lower ( $76.7-77.6^\circ$ ) than obtained in the Sylgard 184 case ( $101^\circ$ ). The resulting films have high surface porosity. Obtained pores size is in the range of 130-330  $\mu\text{m}$ . The mechanical properties of the films were also measured by tensile test. Elongation at break ( $X_R$ ) data suggest that elastic films were obtained using a mixture of GMA and BMA as additives when [AA]: [MA] = 0.3:0.2; 0.25:0.25 and 0.2:0.3,  $X_R$  ranges from 120 % to 320 %, which means that  $X_R$  was 4-11 times higher than commercial PDMS.

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# SYNTHESIS OF NOVEL *N*-ARYL-*N*-POLYSUBSTITUTED THIAZOLYL- $\beta$ -ALANINES

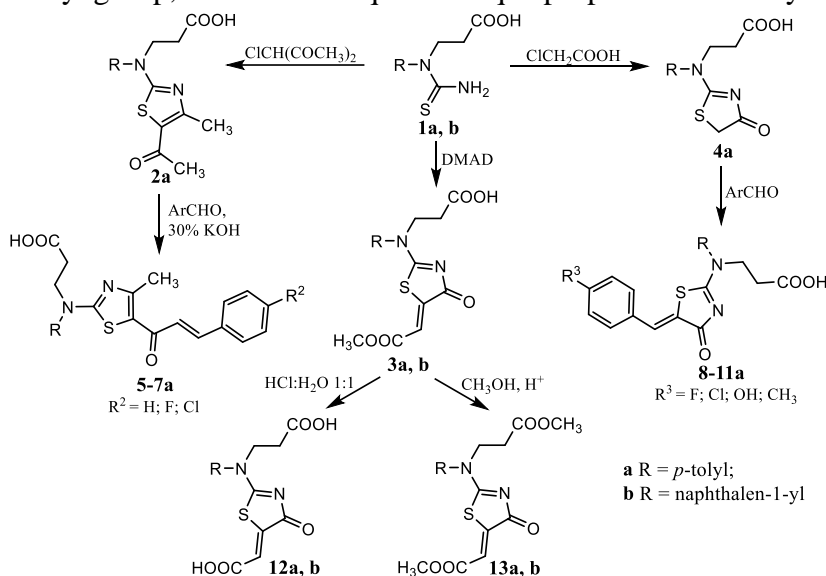
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Thiazole is significant heterocycle with a wide spectrum of biological properties. Its moiety is found in various pharmaceuticals (Tiazofurin, Abafungin, Sulfathiazol), thiazole derivatives show large variety of healing properties and act as anti-tumor, anti-inflammatory, antibacterial and antimicrobial, analgesic, antifungal agents, are selective acetyl Co-A carboxylase-2 inhibitors, neuroprotectors [1–7].

A series of reactions of thioureido acids **1a, b** with carbonyl compounds were carried out to obtain derivatives **2–4** bearing variously substituted thiazole ring. The reactions of thiazole **2a** and thiazolone **4a** with aromatic aldehydes were then investigated. Due to the presence of the acetyl group, thiazole **2a** acquires unique properties for the synthesis of chalcones. Thus, the



Claisen–Schmidt condensation of 4-methyl-5-acetylthiazole derivative **2a** with various aromatic aldehydes in aqueous potassium hydroxide at 80°C for 2 hours provided the target chalcones **5–7a**. 3-((4-Oxo-4,5-dihydro-1,3-thiazol-2-yl)(*p*-tolyl)-amino)propanoic acid (**4a**) containing reactive methylene group was easily transformed into the arylmethylidene scaffold

bearing derivatives **8–11a** by the Knoevenagel reaction. Thiazoles **3a, b** have carboxylic acid and ester functional groups in their structure, therefore the hydrolysis of ester group and esterification of carboxylic fragment were performed which led to the formation of diacids **12a, b** and diesters **13a, b**. All of the synthesized compounds were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, elemental analysis and some representative compounds were characterized by mass spectrometry analysis.

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# SYNTHESIS OF LOW CRYSTALLINE CALCIUM DEFICIENT HYDROXYAPATITE GRANULES

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Calcium phosphate (CaP) based biomaterials have received great interest since they are widely applied for the replacement of diseased or damaged mammalian hard tissues [1-5]. Due to similarity to the inorganic component of natural bone synthetic CaP materials show excellent biological properties in a physiological environment. Currently these artificial bone substitutes are prepared in a form of powders, granules, dense or porous scaffolds, and bioactive coatings on metal prosthesis [6]. Numerous synthesis techniques of CaPs at elevated temperatures have been revealed. However the resulted ceramics exhibit extremely high crystallinity far from natural bone. Consequently, when biomaterial implanted in body it remains in its initial form for the long time. Yet low crystalline material is easier to integrate by surrounding bone tissue during the bone regeneration process [7].

The objective of our study, therefore, was to develop a simple and cost-effective synthesis route for the preparation of low crystalline calcium deficient hydroxyapatite (CDHA, with the formula  $\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5\text{OH}$ ) using a precursor granules. We selected calcium sulphate hemihydrate as starting material. To fabricate CDHA granules we utilized a method based on an incessant dissolution-precipitation reaction eventually resulting in a solid and shaped material consisting of desired phase (Fig. 1).

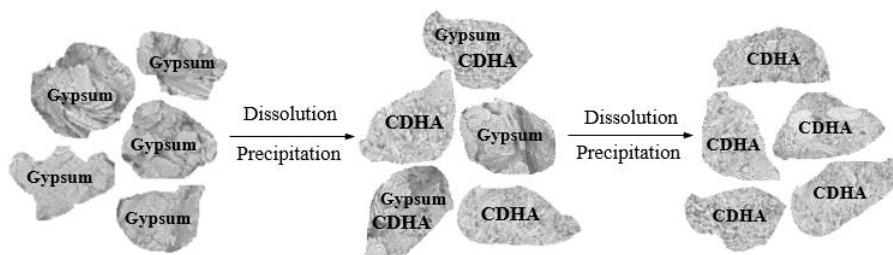


Fig. 1. Schematic representation of dissolution-precipitation reaction.

The monophasic calcium deficient hydroxyapatite granules were synthesized by three slightly different preparative approaches and compared. The obtained synthesis products were characterized by Fourier transformed infrared spectroscopy (FTIR), X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM).

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**DERIVATIVES OF DIMETHOXY-SUBSTITUTED TRIPHENYLAMINE  
CONTAINING DIFFERENT ACCEPTOR MOIETIES AS MULTIFUNCTIONAL  
DYES**

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In recent years, the investigation on solar cells using organic semiconducting derivatives has made considerable advance [1]. Among the promising photovoltaic technologies, dye-sensitized solar cells (DSSCs) have received much attention recently due to their low cost and relatively high efficiency [2].

Most conventional organic dyes possess the push-pull structure of “donor-conjugated bridge-acceptor”. Typically, organic dyes used for efficient solar cells are required to afford intense and broad absorption in the visible spectral region. Aside from donor units, the electron acceptor plays a significant role in the performance control of DSSCs [3]. Introducing an additional electron-donating moiety into derivative of triphenylamine can enhance charge separation, which result in high overall conversion efficiency [4]. Due to the certain peculiarities of the structure of triphenylamine, electron acceptor groups can be introduced. They can affect the molar extinction coefficients, absorption spectra, and the HOMO, LUMO energy levels of the derivatives. Rhodanine 3-acetic acid and cyanoacetic acid were introduced into triphenylamine-based dyes as acceptor moieties [5].

In this paper, easily synthesized dyes based on dimethoxy-substituted triphenylamines were obtained by a Knoevenagel condensation. Two different dyes containing cyanoacrylic acid and rhodanine-3-acetic acid moieties as an electron acceptors were prepared. These dyes show interesting electronic and optoelectronic properties and, as we show, constitute potential candidates to be used in solid state dye sensitized solar cells based using the structure of FTO/TiO<sub>2</sub>/Dye/Spiro-OMeTAD/Ag. In addition, we studied Kerr and two-photon absorption effects of the synthesized derivatives to understand how different acceptor groups influence NLO properties.

#### **Acknowledgement**

This research was funded by a grant (No. S-LZ-19-2) from the Research Council of Lithuania.

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# ELECTROCHEMICAL MODIFICATION OF GRAPHITE FELT IN LEAD(II) NITRATE ELECTROLYTE UNDER FLOW-THROUGH REGIME

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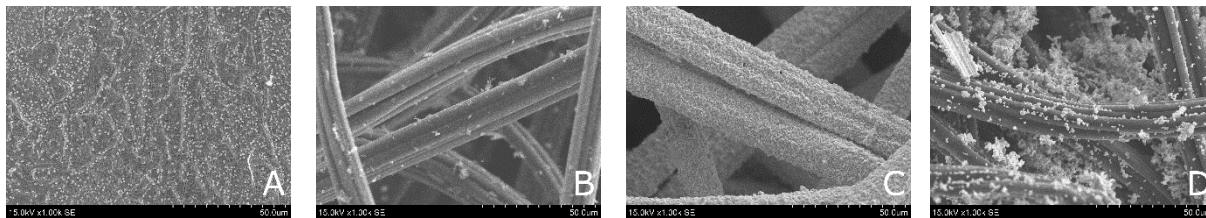
With a push for electrification of (mild, hybrid or full electric) passenger vehicles, new requirement emerged for lead-acid batteries (LAB). Batteries are required to be able to accept and give back a high dynamic charge, operate in partial state-of-charge conditions for as long as possible and, finally, to have an even higher specific power [1]. Because of this, carbon additives in a negative active material of LAB have gained a lot of interest [2]. Moreover, new patents were filed replacing heavy lead grids for lightweight carbon materials [3].

In this study graphite felt (GF) electrodes were modified in a flow-through reactor (FTR) by using an electrolyte, containing 0.5 M  $\text{Pb}(\text{NO}_3)_2$  and 0.1 M  $\text{HNO}_3$  ( $20 \pm 1$  °C). Total electrodeposition time without rest periods at pulsed current was 60 minutes. The flow rate of the electrolyte was maintained at 50 ml/min. for cathodic and anodic sides of FTR. Hydrogen ions permeable membrane was used to separate both compartments of FTR.

Uncontrolled crystal growth was observed when a potentiostatic deposition was applied and this led to rupturing of membrane. Furthermore, current efficiency of deposits decreased when pulsed current under galvanostatic mode was used (Table 1.). Scanning electron microscopy, energy-dispersive X-ray spectroscopy and X-ray diffraction analysis were applied to characterize deposited materials. Pb and  $\text{PbO}_2$  were identified on negatively and positively polarized GF electrodes respectively. Analysis showed a big discrepancy between amount of deposited materials on the inside and outside filaments of GF (Fig. 1). Further research is required in order to optimize electrodeposition of LAB electroactive materials on 3D substrates such as GF.

**Table 1.** Electrodeposition conditions

No.	Current pulse/rest duration, ms	Electrodeposition mode	Total charge, C	Polarity of electrode	Current efficiency, %
1.	None	Potentiostatic $U = 2,5$ V	11513,6	+	9,2
				-	3,5
2.	None	Galvanostatic $i = 25$ mA/cm <sup>2</sup>	298,8	+	83,8
				-	64,6
3.	250/250	Galvanostatic $i = 25$ mA/cm <sup>2</sup>	298,8	+	77,2
				-	42,0
4.	1000/1000	Galvanostatic $i = 25$ mA/cm <sup>2</sup>	298,8	+	71,6
				-	1,7



**Fig. 1.** Scanning electron microscopy images of GF filaments coated with Pb (A – outside, B – inside) and  $\text{PbO}_2$  (C – outside, D – inside) under galvanostatic mode without pulses.

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# PREPARATION AND CHARACTERIZATION OF LUAG AND YAG BASED SCINTILLATION MATERIALS

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Nowadays light based technology is very popular and can be used in different aspects of life. One of the areas, where light based technologies can be used is scintillators, which are made from luminescent materials. That is the base for devices, which are used for detecting and measuring radioactive contamination, monitoring nuclear materials and computed tomography. The most common scintillators are usually made from inorganic compounds. Materials for this case are various alkali-metal halides, alkali earth halides, lanthanide halides, transition metal, post-transition metal, rare-earth oxyorthosilicates or elpasolites [1]. Recently, garnets are one of the most popular materials applied as scintillators. In this work presented garnets are cerium doped yttrium aluminium garnet (YAG:Ce) and lutetium aluminium garnet (LuAG:Ce). Cerium activated scintillators have been investigated for thermal neutron and high energy radiation (X-ray,  $\gamma$  ray) detection [2]. In order to get wide spread application and fast scintillators it is very important to improve their light yield, self-absorption and decay time. These properties could be enhanced by co-doping garnets with boron. It is important that absolute light output is increased due to improved energy migration when garnets are doped with boron, which leads to better performance of scintillators [3]. One of the biggest drawbacks of these phosphors is long decay time. When it is too long, one image could be superimposed on another and this problem may also be solved by incorporation of boron into the garnet structure. Fast response time can allow detection of rare events in particle physics [4].

For this project different compounds were prepared, which could be used in scintillators in order to increase their light yield and self-absorption, also reduce phosphor decay time. The chosen compounds were, YAG:Ce and LuAG:Ce co-doped with boron. Phosphor powder was synthesized by sol-gel method and heated under different atmospheres. Samples were analyzed by x-ray diffraction (XRD), scanning electron microscopy (SEM) and high energy radiation detection was measured. Of course, quantum efficiency, decay times, emission spectrum have also been investigated.

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# SYNTHESIS AND STRUCTURE DETERMINATION OF ALKYL *N*-(*N*-Boc-PIPERIDINYL) PYRAZOLECARBOXYLATES

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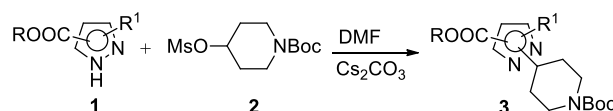
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Natural and synthetic amino acids are used widely as scaffolds and building blocks for the preparation of heterocyclic compounds [1] and peptides [2], including development of DNA-encoded chemical libraries [3]. However, the design and preparation of novel non-natural amino acid collections as building blocks suitable for the development of DNA-encoded chemical libraries is a complex and costly process, whereas the target molecules have to exhibit not only a high degree of structural, and thus functional, diversity in accordance with the principles of diversity-oriented synthesis (DOS), but must also to provide an opportunity to obtain from them drug likeness tripeptide-type or similar molecules, whose structural features correspond the extended Lipinski's rules, including the molecular weight, number of hydrogen bond acceptors and rotatable bonds. The aim of the present work is design and synthesis of a collection of novel constrained amino acid-like building blocks, in their *N*-Boc-protected ester forms, constructed from a pyrazole moiety, possessing carboxyl functional group at any ring carbon atom and a piperidine structural unit, connected to the heterocyclic ring nitrogen atom, as a carrier of a secondary amino functional group.



**Scheme 1.** Synthesis of alkyl *N*-(*N*-Boc-piperidinyl)pyrazolecarboxylates

Treatment of alkyl pyrazole-4- and 5-carboxylates **1** with *N*-Boc-piperidine-4-mesylate **2** in DMF in the presence of Cs<sub>2</sub>CO<sub>3</sub> resulted in the formation of *N*-(*N*-Boc-piperidin-4-yl)pyrazolecarboxylates **3**, as non-chiral amino acid-like building blocks (Scheme 1). The corresponding chiral building blocks were obtained by the alkylation of aforementioned pyrazoles with (*R*)- and (*S*)-*N*-Boc-piperidine-3-mesylates. When non-symmetric pyrazoles were used as starting substrates, the two regioisomeric products were obtained. The discrimination between the formed regioisomers was performed reliably by methods of advanced NMR spectroscopy, in particular by the application of <sup>1</sup>H, <sup>1</sup>H-NOESY, <sup>1</sup>H, <sup>13</sup>C-HMBC and <sup>1</sup>H, <sup>15</sup>N-HMBC experiments.

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# SYNTHESIS AND HDAC INHIBITORY ACTIVITY OF PYRIMIDINE-BASED HYDROXAMIC ACIDS

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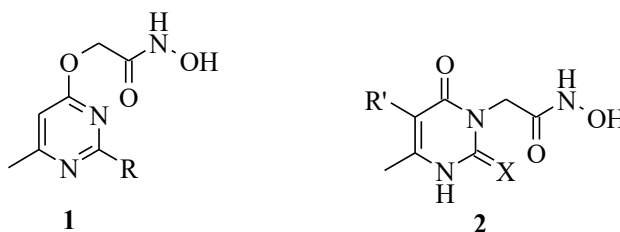
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
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Pyrimidines represent an important group of heterocyclic compounds exhibiting broad spectrum of biological activity [1]. Pyrimidine moiety is a building block for several new drugs introduced to the market every year. Dabrafenib mesylate was approved in 2013 for the treatment of metastatic BRAF-mutant melanoma; macitentan and riociguat – for the treatment of pulmonary arterial hypertension; sofosbuvir – for the treatment of the hepatitis C virus across several genotypes [2]. On the other hand, compounds with moiety of hydroxamic acid serve as antibacterial [3], anti-inflammatory [4], anticancer [5], and other therapeutics. It is also known that pyrimidine-based hydroxamic acids possess diverse biological activities, for example, histone deacetylases (HDACs) inhibitory activity [6]. HDACs are promising targets for anticancer drug discovery and development [7].

Commonly, hydroxamic acids are prepared by coupling activated carboxylic acids with O/N-protected hydroxylamine [4] or by treatment of carboxylic acid esters with hydroxylamine [8, 9].

In consideration of diverse biological properties of this type of compounds and in continuation of our interest in the synthesis of biologically active heterocycles, a series of pyrimidine-based hydroxamic acids **1**, **2** was prepared and evaluated as inhibitors of HDAC8.



R: OH, SCH<sub>3</sub>, SC<sub>2</sub>H<sub>5</sub>, N(CH<sub>3</sub>)<sub>2</sub>, N , NHCH<sub>2</sub>CH=CH<sub>2</sub>, NHCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>; R': H, Br; X: O, S.

The binding affinity of tested compounds towards HDAC8 was measured by fluorescent thermal shift assay.

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# SYNTHESIS AND BINDING ANALYSIS OF CARBONIC ANHYDRASES INHIBITORS – 1, 2-DISUBSTITUTED 6-CHLOROBENZIMIDAZOLE-5-SULFONAMIDES

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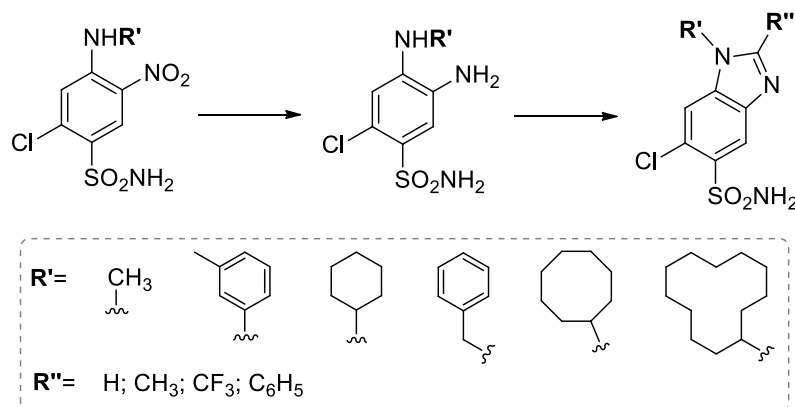
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CAs are family of zinc metalloenzymes that catalyzes the reversible hydration of carbon dioxide. There are twelve active CA isoforms in humans which all have very different subcellular localization, tissue distribution and catalytic activity. Some of these isozymes are potential targets for the development of antiglaucoma, diuretic, antiobesity, anticonvulsant or anticancer drugs [1]. The most common and well-studied class of CA inhibitors is aromatic/heterocyclic sulfonamides. Unfortunately, many sulfonamides synthesized to date possess a lack of selectivity, therefore a great need of potent and selective CA inhibitors remains.

Benzimidazoles occur in a wide variety of pharmaceutically important scaffolds in medicinal chemistry and are key structures in various biologically active compounds. In this study variously substituted benzimidazoles served as sulfonamide scaffold developing new carbonic anhydrase (CA) inhibitors and investigating their substitution effect on the inhibition selectivity.



Synthesis pathways were analyzed and series of 1,2-disubstituted 6-chlorobenzimidazole-5-sulfonamides were synthesized. Binding of synthesized compounds to CA isoforms was determined by the fluorescent thermal shift assay (FTSA).

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## Acknowledgment

To Research Council of Lithuania for Development of Student's Competences from 2014-2020 European Union investment in Lithuania: 09.3.3.-LMT-K-712-10-0212.

# SOL-GEL SYNTHESIS AND SUBSEQUENT DIP-COATING ON SILICON OF YTTRIUM, TERBIUM IRON PEROVSKITES AND YTTRIUM IRON GARNET

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Terahertz spectroscopy for material research is an emerging field in science. New materials need to be created for the construction of devices capable of performing such tasks [1]. Among such materials – yttrium, terbium iron perovskites are promising due to their crystal structure and unique properties, including potential multiferroic behavior [2, 3], as well as yttrium iron garnet which also has been reported to display multiferroic behavior, and can already be used as a tunable microwave filter [4, 5]. In this study, the thin films of these materials were fabricated on silicon substrate using the sol-gel dip-coating [6] method.

The precursor solutions were prepared by dissolving stoichiometric amounts of yttrium and iron nitrates in water, then adding 1,2-ethanediol as a complexing agent. A part of each precursor solution was separated, then evaporated to obtain a gel, which was then heated at 1000 °C to obtain powders. The remaining solution was used for the dip-coating procedure, after mixing it with 3% polyvinyl-alcohol at a ratio of 1:1. The dip-coating was performed on p-type and undoped silicon substrates, with an immersion speed of 85 mm/min, holding time of 10 seconds, and withdrawal rate of 40 mm/min. The dip-coating procedure was repeated 5 and 15 times for different samples, drying the sample at room temperature for 30-60 min. each time, then heating it to 500 °C, holding this temperature for 1 h using a heating rate of 1°/min. After the final layer was deposited, the samples were heated at 1000 °C for 10 h, using a heating rate of 1 °C/min. The prepared coatings were investigated using X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). The powders were also investigated using XRD and thermogravimetric analysis.

The results revealed that while the powders were of a single phase and had well-defined X-ray diffraction peaks, using the same solution for dip-coating yielded coatings of mixed phases.

**Acknowledgements.** This work has been carried out in frame of the project TransFerr. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 778070.

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# KINETIC STUDY OF BENZENE ADSORPTION ON THE SYNTHESIZED CALCIUM ALUMINATES

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Simple aromatic compounds such as benzene, toluene and xylenes are very common by-products of petrochemical industry and are the most commercially significant aromatics. While their negative impact on the environment is widely known, the steadily increasing demand of these materials still raises environmental pollution problems. As one of the most simple and cost-effective decontamination techniques, adsorption usually proceeds without formation of any byproducts and can be reversible. It was always appealing to synthesize optimally operating adsorbents from already available cheap raw materials or industrial waste and avoid depletion of natural resources. Calcium aluminates can be utilized for this purpose as chemically inert, thermally and mechanically resistant as well as high melting point possessing materials [1, 2]. During these experiments, synthesized calcium aluminates were used for the adsorption of benzene. Calcium aluminates were synthesized via sol-gel process with the co-precipitation of calcium and aluminium hydroxides as well as the subsequent calcination for 3 h at 800 °C. Precipitates were calcined in the form of granules (~4x6 mm) with various calcination additives in order to enhance the adsorptive properties of resulting calcium aluminates. In total four different aged (for 7 days) and non-aged samples were produced – with starch, sucrose, activated carbon additives and one remaining blank. As adsorption experiments at 25 °C show, non-aged calcium aluminates possess better adsorptive characteristics 37.750–49.065 mg/g than the aged ones 20.626–32.391 mg/g. The influence of calcination additives was also diverse. When heated without ageing, additives changed the adsorption behavior of calcium aluminates very little with activated carbon additive sample being the exception, because it had an increased capacity for benzene by ~20 %. This probably happened due to the ease of carbon combustion as compared to disaccharide or polysaccharide. During the ageing step, interactions between precipitates took place and new bonds formed which made resulting product more mechanically resistant. In our case, activated carbon interfered with the formation of more stable material and resulted in much worse performance. Being less active than activated carbon, starch and sucrose increased adsorption capacity of calcium aluminate by ~15 %. Kinetic modelling helped to assess adsorptive behavior of calcium aluminates. Linear regression analysis of four common kinetic models was applied: pseudo-first order, pseudo-second order, Vermeulen and intraparticle diffusion (IPD). As calculations indicate, pseudo-second order model matched the experimental data with the highest coefficient of determination ~0.99. Calculated adsorption rate constants  $k_2$  were several times higher for aged adsorbents 0.0072–0.0362 g/(mg·min) than non-aged ones 0.0032–0.0038 g/(mg·min) with the similar tendency for initial rates of adsorption  $h$  – 7.932–15.722 mg/(g·min) and 6.033–9.634 mg/(g·min) for aged and non-aged samples respectively. This indicates adsorption being similar to chemisorption rather than physisorption. In addition, applied IPD model showed multilinear profile of the plot, which indicates that after around 30 min, adsorption becomes heavily controlled by diffusion and uptake of benzene slows down.

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# INVESTIGATION OF THE STRUCTURAL PROPERTIES OF SILVER-INDIUM SELENIDE LAYERS

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Polyester (PES) fabric coated polyvinylchloride (PVC) is one of the most commonly used materials in many modern architecture projects because of its excellent synergy of functionality and aesthetics [1].  $\text{CaCO}_3$  is the dominant filler in the PVC based architectural textile (AT) production because decrease slightly tensile strength, helps increase impact strength, lowers the particle's adhesion to the polymer.  $\text{TiO}_2$  used as a white pigment and UV stabilizer [2]. A composite material consisting of AT modified by thin layers of desirable semiconductors have attracted an interest because of characteristic physical and chemical properties. Before semiconductor layers deposition process, the hydrophobic AT sample requires an initial surface treatment process in order to facilitate its adhesion properties [3].

The aim of this work is investigation of the structural properties of silver-indium selenide layers deposited on PES/PVC architectural textile by chemical bath.

For change chemical composition and physical surface properties of the AT, it previously mechanical roughened and then treated with various etching solutions at different treatment parameters.

The Ag-In-Se layers were synthesized on AT samples as reported in paper [3]. Depending on the exposure time in  $\text{H}_2\text{SeO}_3/\text{Na}_2\text{SO}_3$ ,  $\text{AgNO}_3$  and acidic  $\text{In}(\text{NO}_3)_3$  solutions the colour of AT samples changed from white, through light to dark brown, even black.

Based on the XRD diffractograms analysis we conclude that the PES and PVC polymers are amorphous in nature with only one characteristic broad peak centred at  $2\theta=18.5^\circ$ . In the XRD diffractogram of virgin AT the typical peaks of tetragonal rutile  $\text{TiO}_2$  phase (JCPDS Card File No 84-1284) at  $2\theta$  27.51°, 36.14°, 41.32°, 54.42° and 56.72° are observed. Diffraction peaks at  $2\theta$  angles of 29.50°, 39.53°, 43.20°, 47.65° and 48.61° were indexed to the characteristic peaks of rhombohedral calcite ( $\text{CaCO}_3$ ) (JCPDS Card File No 72-1651). After etching, intensity of all these peaks reduces.

In the XRD diffractogram of  $\text{AgInSe}_2$  layers on AT, the peaks of  $\text{TiO}_2$  and  $\text{CaCO}_3$  similarly more reduces. Appears new peaks at  $2\theta$  32,67°, 33,43°, 41,34°, 42,88°, 43,60°, 48,61°, 51,98°, 53,23°, 54,54°, 63,35°, 64,51° (the orthorhombic  $\beta$ - $\text{Ag}_2\text{Se}$ , JCPDS Card File No. 24-1041), at  $2\theta$  11,42°, 15,32°, 17,15°, 18,45°, 29,34°, 36,66°, 60,51° (the hexagonal  $\gamma$ - $\text{In}_2\text{Se}_3$ , JCPDS Card File No. 72-1469) and at  $2\theta$  31,18°, 31,27° (the hexagonal  $\text{AgInSe}_2$ , JCPDS Card File No. 22-1332) are observed.

The XRD patterns of the crystalline powder, scraped from the AT samples, have high difference in relative intensity. All the reflections indexed to the  $\beta$ - $\text{Ag}_2\text{Se}$ ,  $\gamma$ - $\text{In}_2\text{Se}_3$  and hexagonal  $\text{AgInSe}_2$ .

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# SYNTHESIS OF ANIONIC POLYMER BRUSHES COMBINING RAFT POLYMERIZATION AND EPOXY-THIOL CLICK CHEMISTRY

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Due to pH-responsive properties, molecular brushes with negatively charged side chains are gaining more and more attention [1]. A common method to synthesize such polymer brushes is based on „grafting-onto“ strategy. Using that method, the side chains are grafted onto a pre-established backbone with reactive multiple groups by various coupling reactions, usually, *click* chemistry [2]. Glycidyl methacrylate (GMA) is a versatile monomer [3], which meets the requirements for epoxy-thiol *click* chemistry and can be successfully polymerized via RAFT method (Fig. 1).

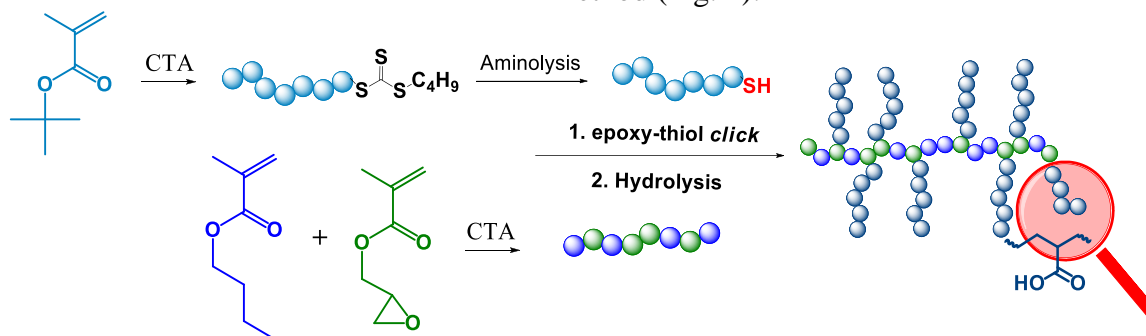


Fig. 1. General scheme of the synthesis of anionic polymer brushes via RAFT and epoxy-thiol *click* chemistry

RAFT polymerization of *tert*-butyl methacrylate (*t*-BMA) was carried out using 4-(((butylthio)carbonothioyl)thio)-4-cyanopentanoic acid as a CTA at various ratios of the CTA to the initiator AIBN. Molecular weight  $M_n$  of the polymers varied from 1600 to 3500, dispersity  $\bar{D}$  being as low as 1.2. The backbone with multiple epoxy groups was synthesized by RAFT copolymerization of butyl methacrylate (BMA) and GMA in *N*-methyl-2-pyrrolidone (NMP) at 65 °C, molar ratio of the monomers to the CTA and AIBN was 300/5/1.  $M_n$  of the copolymer was ~8000,  $\bar{D}$  1.19, and composition BMA/GMA = 48/52 mol%. Substitution of trithiocarbonate end groups of p(*t*-BMA) to thiol groups was performed via simple aminolysis reaction with hydrazine [4].

Epoxy-thiol *click* reactions coupling epoxy groups containing backbone and thiol groups containing p(*t*-BMA) chains were performed in NMP at 70 °C or 80 °C using 4-(dimethylamino)pyridine (DMAP) or triethylamine ( $\text{Et}_3\text{N}$ ) as catalysts. The reactions were monitored by dynamic light scattering (DLS). It was determined, that the reaction rate increased significantly with temperature, irrespective of the catalyst used. During 24 hours, the hydrodynamic radius ( $R_h$ ) of the polymer brushes increased from ~1 nm to 4.5 nm. Anionic polymer brushes containing carboxyl groups were obtained via acidic hydrolysis of *t*-BMA units by trifluoroacetic acid in  $\text{CH}_2\text{Cl}_2$ . Disappearance of *t*-butyl groups was followed by spectroscopic methods (FT-IR and NMR).

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# DIISOCYANATE EXPOSURE TO SOIL AND PERSISTENCE OF HYDROLYSIS PRODUCTS

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High volumes of polyurethane (PUR) foams are used in constructional applications, many of which have direct exposure to soil and ground, such as building foundation repairs, floor lifting, pavement jacking etc. Frequently, a mixture of polyols, blowing agents, prepolymers and isocyanates is injected into soil. Most previous studies investigated the environmental aspects of either the final PUR, or their feedstocks [1]. Little attention was devoted to possible reactions of the PUR injection mixtures with soil constituents, moisture in particular.

Foaming in PUR is a result of CO<sub>2</sub> evolution from isocyanate reaction with water, which is usually available in soil. Injected PUR blends typically contain 30% mol. or higher excess of hexamethylene, toluene or methylene diphenyl diisocyanates, HDI, TDI or MDI respectively. Their reaction with water is much faster than polymerization with polyols, producing PUR foam of desired texture. However, hydrolysis leads to diamines or dianilines, Fig. 1.

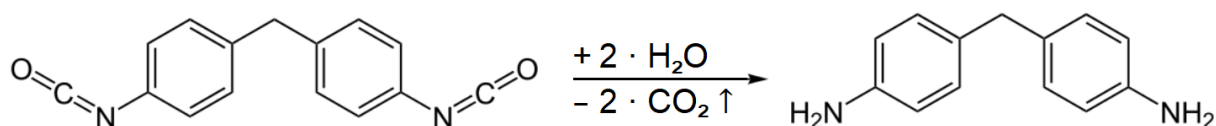


Fig. 1 Example of aromatic diamine production due to exposure of 4,4-MDI diisocyanate to water

Persistence of the hydrolysis products in the environment has not yet received much attention. However, their toxicity, volatility and dissolution appear to be quite significant, Table 1.

Table 1. Lowest reported lethal dosages with approximate vapor pressures and aqueous solubilities of diisocyanate reaction products, as provided in National Institute of Health compilation [2].

Hydrolysis product	CAS number	Diisocyanate	LD50, mg/kg	mmHg at 20°C	Water solubility
2,4-Toluene diamine	95-80-7	2,4-TDI	480 <sup>1</sup>	0.00017	7.5% at 25°C
1,6-Hexane diamine	124-09-4	HDI	180 <sup>2</sup> , 320 <sup>1</sup>	n.d.	246% at 5°C
2,4-Methylene dianiline	1208-52-2	2,4-MDI	3300 <sup>3</sup>	n.d.	n.d.
4,4-Methylene dianiline	101-77-9	4,4-MDI	74 <sup>1</sup> , 264 <sup>4</sup>	2.97	0.1% at 25°C

<sup>1</sup> intraperitoneal (mouse);

<sup>2</sup> intravenous (mouse);

<sup>3</sup> subcutaneous (rat);

<sup>4</sup> oral (mouse).

Although data is only preliminary, it is evident that acute toxicity of diisocyanate hydrolysis products is much higher than that of bisphenols, phthalates and other compounds of concern to human exposure. Even more, their volatility is substantial, as is dissolution in water. If these compounds are in direct vicinity of floor, basement and other residential areas, it is likely that the occupants receive significant intake of diamines and dianilines. Therefore, in addition to PUR toxicity research [3], much more attention should be devoted to the studies of diisocyanate exposure to soil and effects of the reaction products on humans and environment.

## Acknowledgment

The study was funded by programme Inočekiai LT grant 01.2.1-MITA-T-851-02-0029.

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## SYNTHESIS AND APPLICATIONS OF DITHIADIAZOCANES

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Saturated heterocyclic compounds containing two heteroatoms are privileged scaffolds for various pharmaceuticals. Among them, *S,N*-heterocyclic molecular scaffolds appear to be useful in designing potent antipsychotic (e.g. Quetiapine), antiarrhythmic (e.g. Diltiazem), anti-tumor (e.g. Prinomastat) and other biologically active agents [1]. Therefore, they remain to be important synthetic targets.

A number of different *N*-protected-1,5,2,6-dithiadiazocanes has been prepared in few steps from cheap and affordable starting materials. These dithiadiazocanes as an ambipolar synthons comprised of electrophilic sulfur and nucleophilic nitrogen atoms were utilized in a variety of synthetic transformations affording diverse *S,N*-heterocycles important for designing biologically active agents (Fig.1).

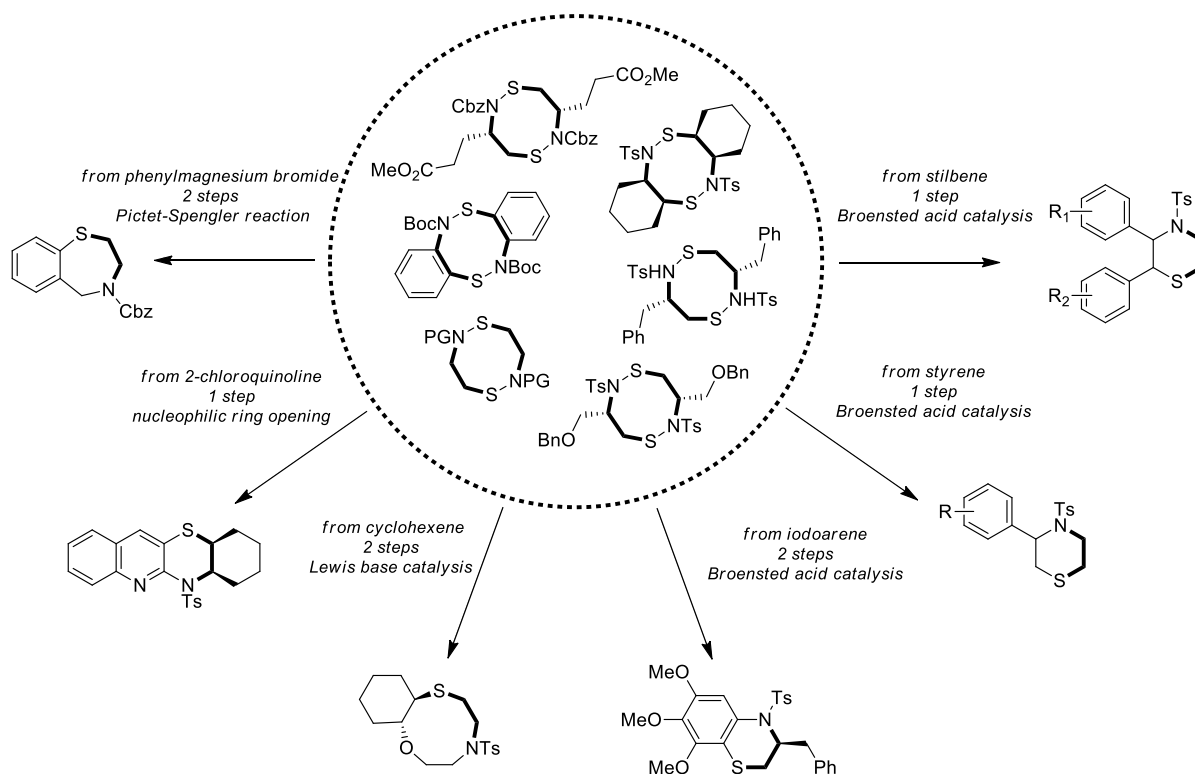


Fig. 1. 1,5,2,6-Dithiadiazocanes and some products available from them.

This research is funded by the European Social Fund under the No 09.3.3-LMTK-712 “Development of Competences of Scientists, other Researchers and Students through Practical Research Activities” measure.

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# ON THE WET CHEMISTRY PREPARATION OF LAYERED DOUBLE HYDROXIDE AND MIXED-METAL OXIDE COATINGS

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Layered double hydroxides (LDHs) are attractive materials that serve as reservoirs and delivery carriers of functional molecules. LDHs are compounds composed of positively charged brucite-like layers with an interlayer gallery containing charge compensating anions and water molecules. The metal cations occupy the centres of shared octahedral whose vertices contain hydroxide ions that connect to form infinite two-dimensional sheets [1-4]. A general chemical formula of LDHs could be expressed as  $[M^{2+}_xM^{3+}_{1-x}(OH)_{2x}A \cdot zH_2O]$ , where  $M^{2+}$  and  $M^{3+}$  are divalent and trivalent metal ions and  $A^-$  is an intercalate anion which compensates the positive charge created by the partial substitution of  $M^{2+}$  by  $M^{3+}$ . After calcination at temperatures from 300 to 600 °C, LDHs are converted to the mixed metal oxides (MMO) with high specific surface area and basic properties. MMO ability to recover the original layered structure is a property known as „memory effect” [5]. LDHs materials have been considered as environmentally friendly containers for active corrosion protection of Mg and Al alloys [6] and heterogeneous catalysts [7]. These LDH materials have the ability to release inhibitors in a controlled manner which can be turned to conform to an increase of the aggressiveness of the environment or corrosion initiation on the metallic substrates.

In this way, the main aim of this study was to investigate Mg-Al-layer double hydroxide seeded growth using co-precipitation and sol-gel method and formation of Mg-Al (mixed metal oxide) with PVA solution on Si and stainless steel substrates through the dip-coating technique. The obtained thin films were characterized by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM).

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# SYNTHESIS OF $(1-x)\text{BaTiO}_3 \cdot x\text{BiMnO}_3$ SOLID SOLUTIONS VIA SOL-GEL METHOD

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Multiferroic materials are special class of solid-state compounds, in which at least two order states such as electric, magnetic, or piezo-elastic coexist [1]. One of the most studied single-phase multiferroic material, which demonstrates coexistence of both ferroelectric and magnetic orders at low temperature, is  $\text{BiMnO}_3$  [2, 3]. The main problem for the preparation of this compound is requirement of high temperature and high pressure during synthesis, while at ambient conditions it cannot be synthesized [3, 4]. Solid solutions containing a substantial amount of  $\text{BiMnO}_3$  could lead to possible synthesis and demonstration of  $\text{BiMnO}_3$ -like properties [5].

In this study, solid solutions of  $(1-x)\text{BaTiO}_3 \cdot x\text{BiMnO}_3$  ( $x = 0.0-0.6$ ) were prepared by sol-gel synthesis method. The appropriate amounts of barium, bismuth and manganese nitrates and titanium isopropoxide ( $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ ) were mixed with citric acid monohydrate and ethylene glycol under continuous stirring for 1.5 h at 90 °C. The ratio between metal ions, citric acid and ethylene glycol was 1:3:10. Next, the solvent was evaporated at 180 °C temperature until the gel was formed. Gel was dried at 180 °C temperature for 12 h. The obtained gel was carefully ground, placed in a ceramic crucible, covered with a cup and heated for 5 h at 1000 °C temperature with a heating rate of 5 °C/min. For the characterization of obtained samples X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and other methods were used. The results obtained showed that the sol-gel synthesis route is suitable for the fabrication of  $(1-x)\text{BaTiO}_3 \cdot x\text{BiMnO}_3$  solid solutions.

**Acknowledgements.** The work has been done in frame of the project TransFerr. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 778070.

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# INVESTIGATION STABILITY OF OXIDIZED spiro-MeOTAD USED IN PEROVSKITE SOLAR CELLS

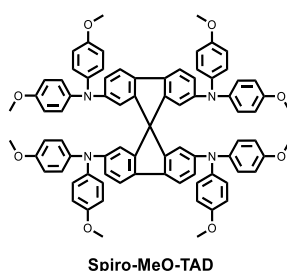
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During past eight years perovskite solar cell (PSC) technology has evolved from a scientific curiosity to a major research subject in the field of photovoltaics. In that short period of time PSC managed to demonstrate remarkable achievements in the power conversion efficiency (PCE), rivalling those of other thin-film technologies as well as silicon photovoltaic devices.[1]

Charge-transporting materials has been developed for use in perovskite solar cells and vast majority of them require the use of chemical doping as an essential step for preparation of efficient devices.[2] Oxidized organic charge-transporting material could be one of the potential weak links in the perovskite solar cell composition. Interestingly, very little investigation is done concerning the oxidized HTMs applied in the PSC and their properties.[3]



In this work the charge-transporting materials, like spiro-OMeTAD and similar compounds, have been investigated under various conditions, in order to estimate stability of the oxidized material and influence of different additives.

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# DETERMINATION OF PHTHALATES IN BOTTLED WATER BY ULTRA-HIGH PRESSURE LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

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1,2-Benzenedicarboxylic acid esters, which are commonly denoted as phthalates, form a group of compounds that is mainly used as plasticisers for polymers such as polyvinylchloride. Despite only a few phthalates are produced at the industrial scale, the annual production of phthalates was estimated by the World Health Organisation to approach 8 million tons [1]. Due to their widespread application phthalates have become ubiquitous in the environment, e.g. Hubert et al. estimated the release of diethylhexyl phthalate (DEHP) to the environment to about 1.8 % of the annual production [2]. In addition phthalates are stable in solution and are able to resist high temperature [3]. Nowadays, due to its massive use and persistent character, phthalates are considered as ubiquitous environmental pollutants. The analysis of phthalates in food matrixes has attracted much attention because of their potential risk to humans' health, including fertility and growth problems. In particular, their analysis in drinking water or beverages, especially those commercialized in plastic bottles, is of importance as a result of the high human consumption and their already mentioned negative effects for health.

In this study, we developed an ultra-high pressure liquid chromatography-tandem mass spectrometry method (UHPLC-MS/MS) for the determination of dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), di-(2-ethylhexyl) phthalate (DEHP) and dioctyl phthalate (DOP) in bottled drinking water after preconcentration by liquid-liquid extraction.

The UHPLC-MS/MS analysis was performed using an Agilent 1290 Infinity LC system coupled with a triple quadrupole 6410 tandem mass spectrometer equipped with an electrospray ionization (ESI) interface. Waters XBridge Shield RP18 column (2.1 × 100 mm, 3.5 μm) was used in the experiments. The column temperature was maintained at 25 °C. The mobile phase flow rate was 0.25 mL/min. A binary mobile phase with gradient elution was used. Solvent A was water with 50 μmol/L sodium acetate, and solvent B was methanol with 50 μmol/L sodium acetate. The gradient program was set as follows: 0-6 min, 30-85% B; 6-7 min, 85-95% B; and 7-25 min, 95% B. The ESI ion source was set for positive ionization. MS/MS detection was performed in multiple reaction monitoring mode. MS/MS experiments were performed by fragmentation of the sodium adduct ion [M+Na]<sup>+</sup> for each phthalate.

Two extraction techniques, namely solid-phase extraction and liquid-liquid extraction, were tested to extract and preconcentrate the phthalates from water samples. Liquid-liquid extraction with hexane showed better extraction performance of all five phthalates with good recovery. The limits of quantification for all 5 analytes were between 10 to 20 ng/L. Good linearity was obtained with R<sup>2</sup> > 0.99 for all phthalates.

Twelve samples of water in plastic bottles from different commercial brands were analysed. The results showed that all brands of bottled water were contaminated with DBP and DEHP. The determined phthalate concentrations were below the maximum permissible levels.

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# SYNTHESIS OF POTENTIAL HSP90 AND HDAC MULTITARGET INHIBITORS

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Inhibition of histone deacetylases (HDACs) is a proven way to treat cancer [1] and compounds inhibiting HSP90 (Heat Shock Protein) shows promising anti-tumor properties as well [2]. We propose that it is possible to combine active fragments of inhibition to yield small-molecule drugs with improved therapeutic and side effect profile [3]. We chose known pharmacophores for the task - resorcinol moiety was selected to target HSP90 and hydroxamic acid functional group to target HDACs.

The first synthesis (Figure 1) was started from commercially available 2,4-dihydroxybenzoic acid **1**, which was converted to methyl ester **2**. In the following reactions compound **2** was substituted in the 5th position to give compounds **3**. Introduction of hydroxamic acid functional group gave desired products **4** in good yields.

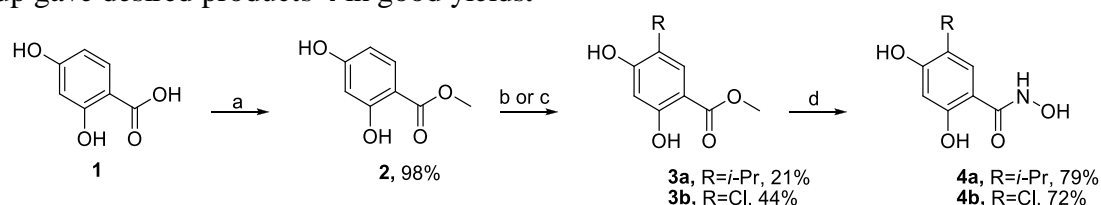


Figure 2. Syntheses of 5-substituted-2,4-dihydroxyphenylcarbohydroxamic acids. Reagents and conditions: a) H<sub>2</sub>SO<sub>4</sub>, MeOH, 30h, reflux, b) i-PrBr, AlCl<sub>3</sub>, DCM, reflux, c) SO<sub>2</sub>Cl<sub>2</sub>, DCM, 2h 0°C, 20h 20°C, d) NH<sub>2</sub>OH·HCl, NaOH, H<sub>2</sub>O, 3h 0°C, 12h 20°C.

The other structures we chose were benzimidazole derivatives **10** (Figure 2). Aldehydes **7** were made from starting materials **5** and **6**. Combination of **7** and **8** gave benzimidazole derivatives **9**. Compounds **9a**, **9b** were converted to hydroxamic acids **10a** and **10b** respectively.

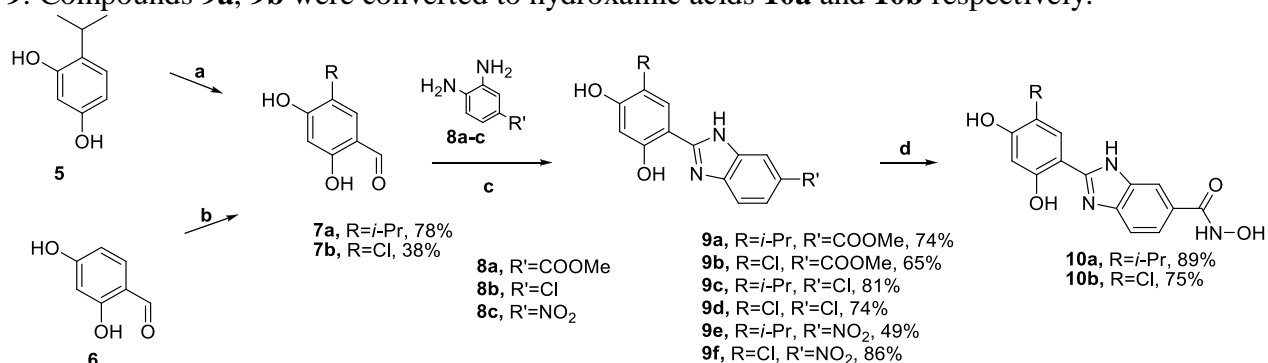


Figure 3. Syntheses of 2-arylbenzimidazo-5-carbohydroxamic acids. Reagents and conditions: a) POCl<sub>3</sub>, DMF, 1h 0°C, 1h 50°C, b) NCS, HCl, CHCl<sub>3</sub>, 4h, reflux, c) Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, DMF, 4h 80°C, d) NH<sub>2</sub>OH·HCl, NaOH, H<sub>2</sub>O, 3h 0°C, 12h 20°C.

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# INFLUENCE OF CALCINED CLAY ON THE EARLY HYDRATION OF ANHYDRITE BINDING MATERIAL

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Anhydrite binding material (ABM) consists of insoluble anhydrite, which is produced by burning natural gypsum or industrial gypsum at 500–700 °C temperature, and additives that speed up the hydration process [1]. Cupola dust, clay, glass and other materials can be used as activators [2-5]. The aim of this research was to determine the effect of calcined clay on the early hydration of anhydrite binding material.

Flue gas desulfurization gypsum (FGD gypsum) (Ltd “Lietuvos elektrinė”, Lithuania) and clay (Kruna location, Lithuania) were used in this research. Clay was calcined for 1 hour at temperatures of 500, 600, 700 and 800 °C in a muffle furnace. Calcined clay was mixed with anhydrite obtained by burning FDG gypsum 30 min at 700 °C temperature. The amount of additive in the system was 5 wt% and 10 wt%. Raw materials and hydration products were characterized by XRF, XRD, FT-IR and other methods. The physical-mechanical properties of ABM were determined according to the European Standard EN 196-3, EN 196-1.

It was determined that the amount of calcined clay didn't make a positive impact on the properties of anhydrite produced at 700 °C. Increasing amount of additive, the chemically combined water content in hydrated ABM at its early age (after 14 days) decreased from 10.23 to 9.35 %, when clay calcined at 600 °C was used. Increasing amount of calcined clay the compressive strength of ABM decreased as well. According to the results, increasing calcination temperature of clay the chemically combined water content after 14 days decreased from 12.66 to 8.98 % and compressive strength of ABM decreased from 2.36 to 0.85 MPa, respectively, when 5wt% of calcined clay was used. Thus it is possible to state that the amount of calcined clay and calcination temperature of clay didn't have a large influence on the properties of anhydrite binding material at its early age.

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## SYNTHESIS OF SHIFF BASES FROM 3-[(4-METHOXYPHENYL)AMINO]PROPANEHYDRAZIDE AND THEIR ANTIBACTERIAL ACTIVITY

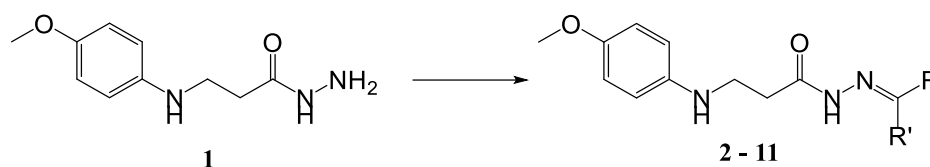
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Antimicrobial resistance has become a global challenge of the contemporary society due to the overuse of antibiotics and appearance of multidrug-resistant strains. The World Health Organization has stated that resistance to common bacteria has reached alarming levels [1]. Thus synthesis of new antibacterial agents is of crucial importance.

Compounds **2–11** were synthesized by condensation reaction of 3-[(4-methoxyphenyl)amino]propanehydrazide and corresponding mono- and disubstituted ketones [2-3] (Scheme).



No	2	3	4	5	6	7	8	9	10	11
R	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
R'										

**Scheme.** Synthesis of Schiff bases **2–11**.

Screening of the antibacterial activity of the synthesized compounds **2–11** at concentration 1 mg/ml has revealed that *N'*-(1-(furan-2-yl)ethylidene)-3-((4-methoxyphenyl)amino)propanehydrazide (**2**) and 3-((4-methoxyphenyl)amino)-*N'*-(1-(naphthalen-2-yl)ethylidene)propanehydrazide (**11**) are the most active against *E. coli* with inhibition zones 0.98 and 0.97 cm, respectively. The inhibition zone of 3-((4-methoxyphenyl)amino)-*N'*-(1-phenylpropylidene)propanehydrazide (**6**) against *X. Campestris* was 0.98 cm, whereas 3-((4-methoxyphenyl)amino)-*N'*-(1-(4-nitrophenyl)ethylidene)propanehydrazide **8** was the most active against *R. Radiobacter* (0.9 cm).

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### Acknowledgment

This research was funded by the European Social Fund under the activity "Development of students' ability to perform R&D activities" of the measure No 09.3.3-LMT-K-712 "Development of scientific competence of scientists, other researchers and students through practical research activities".

# SURFACE MODIFICATION OF VARIOUS MORPHOLOGY GdPO<sub>4</sub> PARTICLES USING CATIONIC BRUSH COPOLYMERS

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Development of both micro and nano sized particles with different structure and morphology has increased significantly in recent years as morphology could be responsible for some of physicochemical properties of particles. Rare-earth doped –micro and –nano orthophosphate particles are promising host materials as they possess good both chemical and thermal stability, appropriate luminescent properties and are already applied as luminescent phosphors, down/up-conversion materials, catalysts and so on [1, 2]. As phosphates are biologically inert host – these particles show high potential to be applied in bio-related fields such as MRI contrast agents, bio-labeling, drug delivery etc. [3]. However, applicability of such particles is limited by poor stability in aqueous solutions. The usage of various commercial surfactants (eg. oleic acid, TRITON, TWEEN etc.) cannot ensure desired stability of LnPO<sub>4</sub> particles. It is known that polymeric brush electrolytes have high potential to surface modification and stabilization of other nanoparticles (eg. SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> etc.) [4, 5] and in our case the usage of non-linear polymeric materials could be a solution.

In this study, we present the synthesis of cationic brush polyelectrolytes and their use in stabilization of GdPO<sub>4</sub> particles in aqueous media. Polymers of various compositions were synthesized via RAFT polymerization route. SEC equipped with triple detection (RI, DP, RALS, LALS) were used to determined molecular parameters ( $M_n$ ,  $M_w$ ,  $M_w/M_n$ ). Thus exact composition of synthesized polymers were determined using combined spectroscopic methods (NMR, IR, RAMAN). Cationic brush polymers were used to improve stability of aqueous GaPO<sub>4</sub> particle dispersion. Firstly, the IEP points of different morphology GdPO<sub>4</sub> particles (nanorods, nanoprisms, nanospheres) were found by measuring zeta potential of bare particle dispersions under various pH values. The oppositely charged particles (negatively charge in alkaline media pH ~ 10) in dispersion were treated by cationic polyelectrolytes of different compositions. The concentration and composition effects of used polymers on change of particle surface potential and stability (DLS measurements) in dispersions were investigated and presented in this work.

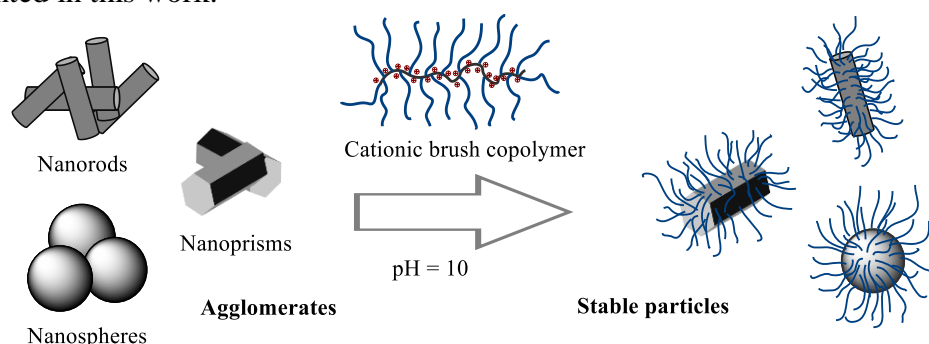


Fig. 1. Graphical illustration of GdPO<sub>4</sub> with different morphology (nanorods, nanoprisms, nanospheres) stabilization by using cationic brush copolymers

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# THE INFLUENCE OF COBALT IONS ON COMPOUNDS FORMATION PROCESS IN CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O SYSTEM

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## Introduction

Recently, it was determined that heavy metals (copper, lead, cadmium and etc.) can enter into the calcium hydroalumosilicates crystal structure [1-3]. Wherefore, calcium hydroalumosilicates have attracted a widespread interest in potential applications, such as precursors to catalysis processes [4]. Natural calcium hydroalumosilicates are used in many processes; however, a wider application is limited by their physico-chemical properties [5-6]. Other important factors which limit the use of natural compounds are the variable crystal structure and probable presence of impurities [1; 7] because, the specific product properties can be controlled during the synthesis. For this reason, the aim of this work is to examine the influence of cobalt ions on compounds formation process in CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O system under hydrothermal conditions.

## Materials and methods

Dry primary mixture with molar ratio of CaO/SiO<sub>2</sub> = 1.5; Al<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>+SiO<sub>2</sub> = 0.08 was mixed with Co(NO<sub>3</sub>)<sub>2</sub> solution (c = 10 g Co<sup>2+</sup>/dm<sup>3</sup>) to reach the solution/solid ratio of the suspension equal to 10.0. The hydrothermal synthesis was carried out in unstirred suspensions, under saturated steam pressure at 200 °C temperature for 0-72 hours (the temperature was reached within 2 h).

## Results and discussion

It was determined that after 0 hours of isothermal curing (only: the temperature was reached within 2 h) at 200 °C, semi-crystalline calcium silicate hydrates (C-S-H (I), C-S-H (II)) and CoO were formed. Also, the basic reflections of partially unreacted gibbsite was observed in X-ray diffraction patterns. When hydrothermal synthesis is extended to 4 h, gibbsite reacts fully, because typical diffraction peaks characteristic to this compound are not detected. By prolonging isothermal treatment duration from 8 h to 72 h it was observed that whole quantity of CoO was fully reacted with C-S-H and formed calcium cobalt silicate together with another products. The results of liquid phase analysis showed that all Co<sup>2+</sup> ions were penetration in the synthesis products under all experimental conditions. The previous results were confirmed by XRD, STA, and SEM analysis.

## Acknowledgement

This research was funded by a grant (No. MIP – 17-92) from the Research Council of Lithuania.

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# BIOCOMPATIBLE FILMS FROM VINYLPIRROLIDONE, HYDROXYETHYL METHACRYLATE AND POLY(DIMETHYL SILOXANE) COPOLYMERS FOR TISSUE ENGINEERING

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Tissue engineering is a rapidly expanding interdisciplinary field involving biomaterials science, cell biology, cell-material interactions and surface characterization. Research in this field aims to restore, preserve, or enhance tissue functions [1]. Poly(dimethyl siloxane) (PDMS) – is widely used as synthetic silicon elastomer in biomedicine. This polymer shows great potential as biocompatible component that is nontoxic, elastic, resistant and gas permeable [2]. However, it has negative attributes like its hydrophobicity, which causes friction in human body and interferes with cell culture reproduction. PDMS could be modified to reduce its hydrophobicity. One of the ways to modify PDMS is copolymerization with hydrophilic monomers. Previously good results were obtained when diepoxy-PDMS was attached to acrylic acid-based copolymers via OH-groups of 2-hydroxyethyl methacrylate (HEMA) units [3].

Herein, hydrophilic copolymer from vinylpyrrolidone (VP), buthyl methacrylate (BMA) and HEMA was modified with diepoxy-PDMS and glycidyl methacrylate (GMA). UV curing was used for obtaining films from modified copolymers via photopolymerization by initiation with photoinitiator IRG651. The structure of modified copolymers was proven by FT-IR, SEM with high current mode for EDS and <sup>1</sup>H NMR. The most insoluble and swellable films were obtained when the initial monomer ratio [VP]:[BMA]:[HEMA]:[DE-PDMS] was 1:0.4:0.3:0.15. This film was shown high Young's modulus (1.11 MPa) and relative elongation at break (235.1%). Obtained films exhibit good wettability in comparison to commercial PDMS film (Sylgard 184), their water contact angle was lower (66.1-89.2°) than obtained in the Sylgard 184 case (101°). Depending on the amount of diepoxy-PDMS used during the synthesis, the Si content in the formed films was varied in the range from 1.6 to 8.8 %. Good mechanical properties of the films were obtained due to the introduction of the siloxane units as hydrophobic grafts to the backbone of hydrophilic copolymer. Mechanical properties of obtained films were similar to blood vessels of living organisms.

Obtained copolymers are suitable for formation by 3D printing technique. The shortest curing time (30 s) was achieved by forming a film with a 3D printer using the initial monomer ratio [VP]: [BMA]: [HEMA]: [DE-PDMS] = 1: 0.4: 0.2: 0.1 and GMA as an additive.

Suitability of formed films for tissue engineering was examined by biocompatibility study. The biocompatibility of the formed films with the myogenic cells in rats is greater than that of commercial PDMS.

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# OPTICAL CHARACTERIZATION OF SILVER-INDIUM SELENIDE LAYERS ON ARCHITECTURAL TEXTILE

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Polymers modified with the inorganic materials combine the functionalities of polymer matrices with the unique features of inorganic semiconductor. Polyester (PES) fabric coated with polyvinylchloride (PVC) is one of the most commonly used architectural textiles (AT) in many modern architecture projects [1]. There is currently a great interest in  $A^I B^III C^VI_2$  semiconductor particles, for their importance as light harvesting materials [2]. The new structure could improve the efficiency of solar tracking made by photovoltaic panels. In present investigation, we synthesized Ag-In-Se layers on AT (PES/PVC) surface. XRD patterns showed a complex AT/Ag-In-Se layers crystalline composition with orthorhombic  $\beta$ -Ag<sub>2</sub>Se (JCPDS#24-1041, hexagonal  $\gamma$ -In<sub>2</sub>Se<sub>3</sub> (JCPDS#72-1469) and hexagonal AgInSe<sub>2</sub> (JCPDS#22-1332) peaks. The obtained composites characterized by UV-Vis light diffuse reflectance spectra (DRS) (Fig. 1). This analysis is one of the most important optical techniques that permit to describe the electronic behaviour present in the solid structure, giving information about the electronic transition of the different orbitals of a solid, through the absorption spectra. From the DRS spectra band gap ( $E_g$ ) determined by applying the Kubelka-Munk method [3-4]. By plotting  $(\text{hvK})^{1/2}$  for indirect allowed transitions versus  $\text{hv}$  (Fig. 2) the  $E_g$  value is determined by the intercept in the x-axis.

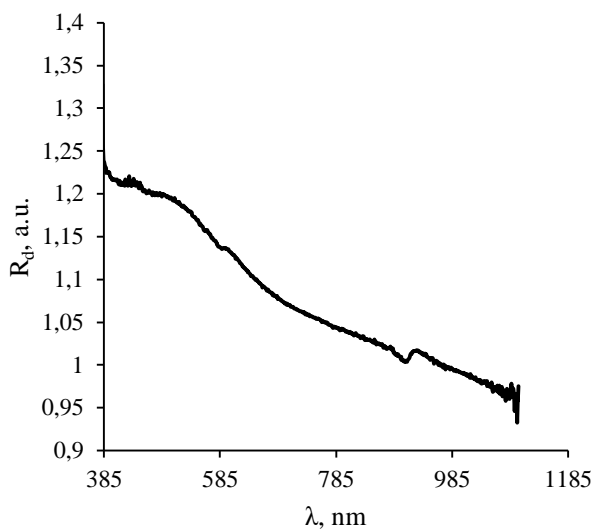


Fig. 1. UV-vis light diffuse reflectance spectra of AT/Ag-In-Se composites

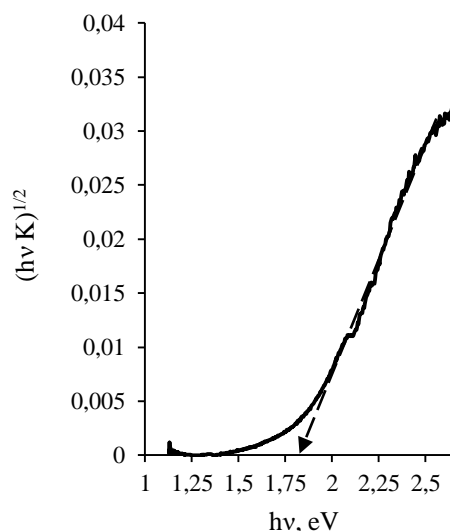


Fig. 2. Band gap calculation from DRS spectra by Kubelka-Munk method

The obtained  $E_g$  are promising from the point of view of the versatility of this material for optoelectronic applications.

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# AGGREGATION-INDUCED EMISSION TETRAPHENYLETHENE TYPE DERIVATIVES FOR BLUE TANDEM ORGANIC LIGHT-EMITTING DIODES

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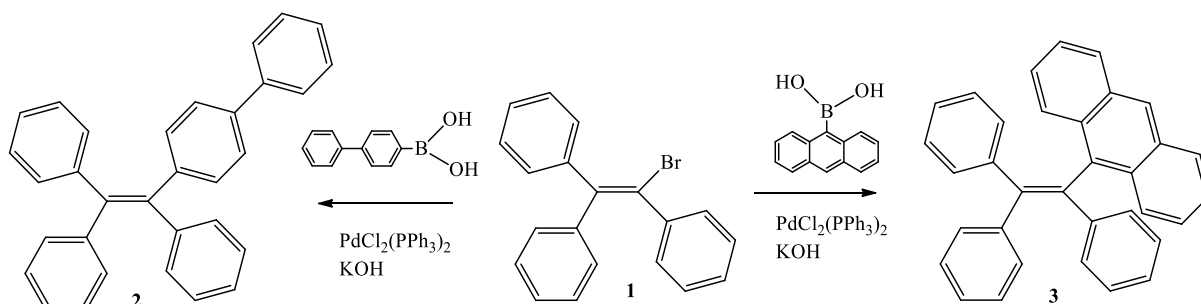
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Organic light-emitting diodes have been seen as one of the most important solid-state sources, and are widely used as the primary display in cellphones and other portable devices. Compared to other competing technologies, OLEDs stand out because of their superior display quality and flexible properties allowing them to meet a variety of application needs. However, for any given commercial application, OLEDs still have to pursue higher device efficiency and operational stability. This has driven the aggressive development of luminogenic compounds, including exciplex [1], thermally activated delayed fluorescence [2], and aggregation-induced luminescence emitters [3].

The synthesis of the triphenylethylene type compounds with biphenyl or anthracenyl fragments (2 and 3) was carried out by a one step synthetic route as shown in Scheme 1.



Scheme 1. Synthetic route of tetraphenylethene type derivatives **2** and **3**.

Synthesized compounds possess bipolar transport capabilities, high thermal stability, and strong sky-blue AIE emissions. Both compounds **2** and **3** were selected as emitters to investigate their electroluminescence applications. The optimized non-doped sky-blue organic light-emitting diodes (OLEDs) with **2** and **3** exhibited respective maximum efficiencies of 3.8% (8.8 cd/A) and 2.2% (4.0 cd/A), correspondingly. Furthermore, a tandem device architecture was used to improve device efficiency. Through adopting the specific designs of the intermediate charge generation layer structure and the corresponding device architecture, respective peak efficiencies of 8.2% (19.4 cd/A) and 4.6% (9.5 cd/A) were obtained in tandem devices with **2** and **3** emitters together with slight efficiency roll-off.

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**Acknowledgment.** The authors gratefully acknowledge financial support from the Ministry of Science and Technology of Taiwan (MOST 107-2221-E-155-028 -) and from the Research Council of Lithuania (S-MIP-17-64).

# ELECTROPHORETIC DEPOSITION OF GRAPHENE OXIDE-SILVER COMPOSITE COATINGS

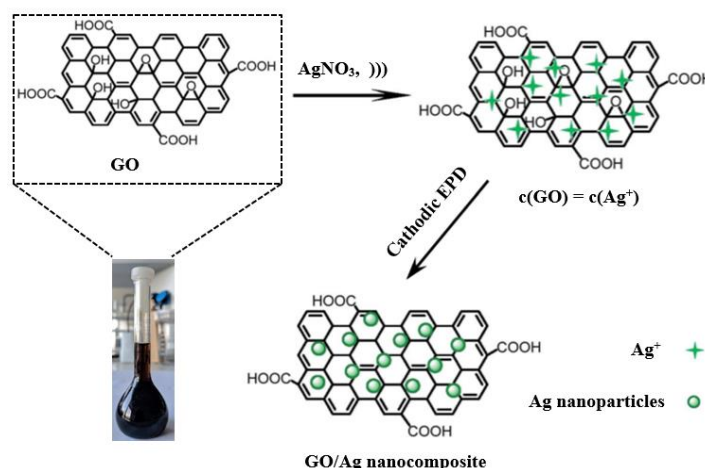
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In recent years, electrophoretic deposition (EPD) has been widely employed to produce composite materials for coatings. Especially, this versatile, fast and low-cost technique has been shown to be effective for manipulating graphene layers in liquid suspensions with the aim to produce graphene-based composite materials for catalytic, sensing, energy storage and environmental applications [1]. EPD of graphene oxide (GO) nanosheets on metals is an attractive coating method but the negatively-charged GO only allows the anodic EPD process, which makes it difficult to achieve high-quality coating layers due to oxygen gas bubbling and electrochemical oxidation of metal substrates [2]. However, GO nanosheets with dimensions in the range of a few micrometers have an atomically flat and big surface, which could be charged positively by adsorption of metal ions on it. Silver nanoparticles have been proposed as a great catalyst and electrocatalyst, owing to their excellent conductivity and large specific surface area [3]. Thus, in this work, was imposed the positive charge to GO sheets by using  $\text{Ag}^+$  ions and successfully carried out the cathodic EPD of GO/Ag nanocomposite coating on a copper electrode surface.

The electrophoretic deposition process (Fig. 1) was carried out at room temperature in an aqueous solution which contained different and equal to each other concentrations of GO and  $\text{Ag}^+$  ions  $c(\text{GO})=c(\text{Ag}^+)$ : 1,25, 2,5 and 5,0 mM. Two copper plates (20×20×0.5 mm) were used as anode and cathode. The electrodes were immersed vertically into the suspension at a gap of 1 cm from each other. A constant DC voltage (2 V) was applied for an optimized time of 1 min. Obtained GO/Ag nanocomposite coatings were rinsed with distilled water and dried overnight at room temperature. The nature of GO/Ag nanocomposites was characterized by using Fourier transform infrared (FTIR), X-ray diffraction (XRD), UV-visible absorption spectroscopy and scanning electron microscopy (SEM) analyses.



**Fig. 1.** Schematic illustration of GO/Ag nanocomposite preparation via cathodic electrophoretic deposition (picture adapted from [1]).

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## COPPER-DOPED TIN(II) SELENIDE THIN FILMS

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Tin selenide is a binary chalcogenide, which is highly valued for its properties such as non-toxicity, low antireflection value and high absorption coefficient. As semiconductor, with narrow optical band gap between 1.0 and 1.1 eV, it could be used in photovoltaic devices such as solar cells [1].

There are many techniques for deposition of tin selenide films on substrate surface, for example spray pyrolyses, molecular beam epitaxy, pulsed laser deposition and else. All these methods require sophisticated instruments or conditions [2]. In this work tin selenide layers were formed on polyamide 6 surface by simple sorption diffusion method which consists of two stages: selenization and treatment with tin(II) precursor solution (Table 1).

**Table 1.** Conditions of tin selenide layer formation

Selenization			
Solution	Temperature, °C	Time, min	
0.1 mol/l selenotrithyonate in HCl 0.1 mol/l	60	120	
Treatment with tin(II) precursor solution			
Concentration, mol/L	Ligand	pH control agent	pH value
Supersaturated	Na <sub>2</sub> H <sub>2</sub> EDTA	NH <sub>3</sub> · H <sub>2</sub> O	12.61

Nowadays a great attention is paid for ternary layers such as Cu<sub>3</sub>SnS<sub>4</sub> or CuInSe<sub>2</sub>. Incorporation of other element into primary semiconductor layer has a possibility to change its properties [3]. In this work tin selenide layer was modified by copper incorporation. Due to this polyamide sheets were immersed in Cu(I) and Cu(II/I) precursors solutions. Copper(I) precursor solution was prepared by copper(II) sulfate reduction with hydroxylamine sulfate. Color of solution changed from blue into clear solution. Copper(I/II) precursor solution was prepared by copper reduction with hydroquinone. Solution color changed from blue to green.

After treatment polyamide 6 sheets with tin(II) and copper precursor solutions, elemental constitution was studied by energy-dispersive X-ray spectroscopy (EDX) and surface analysis was done by atomic force microscopy (AFM).

### Acknowledgements.

This research is funded by the European Social Fund under the No 09.3.3-LMT-K-712-10-0230 “Development of Competences of Scientists, other Researchers and Students through Practical Research Activities” measure.

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# SYNTHESIS AND PROPERTIES OF CARBAZOLE-BASED DERIVATIVES AS EXCIPLEX FORMING SYSTEMS

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Electroactive organic compounds are used as light-emitting materials for optoelectronic devices such as light-emitting diodes, solar cells and electrophotographic photoreceptors [1, 2]. Carbazole-based compounds have advantageous characteristics such as thermal and electrochemical stability, high electron/hole conductivity and efficient luminescence [3]. Due to these properties carbazole fragments were chosen for this study. The synthesis and properties of carbazole derivatives bearing trifluorophenyl-acceptor group **1-3** are presented (Fig 1). The materials **1-3** were synthesized by Ullman-coupling and Suzuki-coupling methods.

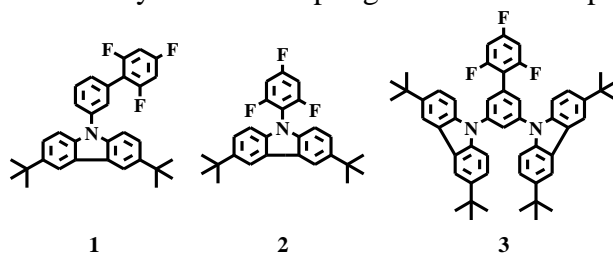


Fig. 1. Structures of **1-3**.

The structures of the synthesized compounds were proved by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and mass spectrometry.

The behavior on heating of compounds **1-3** was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under a nitrogen atmosphere. A temperature ranging from 201 °C to 369 °C of compounds **1-3**. Compound **3** demonstrates the highest thermal stability (369 °C). The ionization potentials of the derivatives were estimated by cyclic voltammetry (CV). They were found to be comparable and ranged from 4.85-5.25 eV. The electron photoemission spectra of layers of the derivatives showed the ionization potentials of 5.94-6.19 eV.

The fluorescence emission wavelength of compounds is in the region of green-blue light. Triplet energy values ranging from 2.58 eV to 2.79 eV were determined from phosphorescence spectra. Because of favourable triplet energy values these compounds were tested as exciplex forming systems with acceptor 2,4,6-tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine [4].

**Acknowledgment.** This research was funded by the European Social Fund under the No 09.3.3-LMT-K-712 “Development of Competences of Scientists, other Researchers and Students through Practical Research Activities” measure.

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# GLUCOSE BIOSENSOR BASED ON GLUCOSE OXIDASE AND POLYANILINE NANOFIBERS

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Polyaniline (PANI) is one of the mostly studied organic conducting polymer that has been developed over the past 30 years due to its low-cost, ease of synthesis and attractive electrochemical properties [1]. One-dimensional (1D) PANI nanostructures were recently employed in biosensors and biofuel cells fabrication [2]. PANI nanostructures usually serve as a biocompatible matrix for immobilization of enzymes [3] and for the fabrication of glucose biosensors [4] based on enzymes glucose oxidase (GOx) and glucose dehydrogenase [5]. The main aim of this research was to investigate the influence of PANI layer on the sensitivity, stability and linear detection range of glucose biosensor.

In this work an amperometric biosensor suitable for the determination of glucose was developed. Lateral surface of the graphite rod (GR) electrode was isolated with a silicone tube. PANI nanofibers which were chemically synthesized through interfacial polymerization, were deposited on GR electrode surface. GOx solution was distributed on the PANI nanofiber layer. Furthermore, the prepared electrode was fixed over the glutaraldehyde solution for the crosslinking of enzyme. Michaelis–Menten kinetics of the designed biosensor in the presence of N-methylphenazonium methyl sulphate as a redox mediator was investigated. In addition, the stability of fabricated biosensor was evaluated. Lastly, the influence of PANI nanofiber layer on analytical characteristics of amperometric glucose biosensor was investigated.

## Acknowledgments

This research was funded by the European Regional Development Fund according to the supported activity ‘Research Projects Implemented by World-class Researcher Groups’ under Measure No. 01.2.2-LMT-K-718.

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# SYNTHESIS AND INVESTIGATION OF THIOXANTHONE BASED COMPOUNDS EXHIBITING TADF, AIEE AND RTP EFFECTS

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For the past few decades organic light emitting diodes (OLEDs) have been a widely researched field in organic optoelectronics. A great deal of research has been made in effort to achieve highly efficient materials for various high-resolution OLED displays and lightning devices [1]. Thermally activated delayed fluorescence (TADF) emitters have been recently attracting much attention due to their ability to push the internal quantum efficiency of OLEDs up to 100% of their theoretical value [2]. TADF enables the possibility of harvesting both singlet and triplet excitons due to very low energy gap between excited singlet and triplet states.

Recently, two different thioxanthone based emitters were published [3]. They showed good thermal stability, aggregation-induced emission enhancement (AIEE) and TADF [3]. OLEDs containing thioxanthone-based materials characterized by efficient TADF showed external quantum efficiencies ranging from 11 to 21.5% [3,4].

In this work, four thioxanthone based derivatives with different donor fragments were synthesized and their thermal, electrochemical, photophysical properties were investigated. It was discovered that some of the aforementioned materials not only exhibited TADF and AIEE effects, but also showed room temperature phosphorescence. OLEDs with maximum external quantum efficiencies up to 8% were fabricated using thioxanthone-based derivatives.

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# CHAIN EXTENSION OF CAPROLACTONE AND ETHYLENE GLYCOL MACRODIOLS INTO HYDROXY-TERMINATED POLYURETHANES

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Polyurethane (PU) plastics are widespread in various areas such as adhesives, coatings, synthetic leather, etc. [1]. Frequently, PU plastics are synthesized from two components: 1) macrodiols and 2) isocyanates, whose reactions form urethane linkages [2]. The macrodiol must contain two OH groups with a polyether, polyester, hydrocarbon, polycarbonate or other type of spacer chain in between. Quite often, the macrodiol is pre-reacted with diisocyanates for chain extension and only then cross-linked into the final PU plastic. Resulting properties also depend on molecular weights, degree of crystallinity and morphology of PU polymers [3] in addition to the consequences of many side reactions, such as CO<sub>2</sub> evolution.

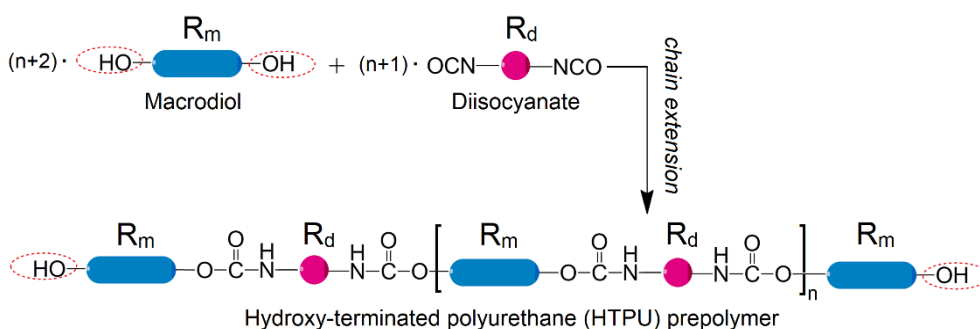


Fig.1. Synthesis scheme of HTPU prepolymers. R<sub>m</sub> = PCL or PEG and R<sub>d</sub> = TDI or HDI. Spacers not to scale.

The aim of this study was to synthesize a hydroxy-terminated PU (HTPU) prepolymer that can be further used as an OH-component for two-component PU adhesives. The HTPU prepolymers were prepared by solvent-less polyaddition of macrodiols and diisocyanates. Polycaprolactone (PCL) adduct with ethylene glycol (M<sub>n</sub>=2000 g/mol) or polyethylene glycols (PEG) of M<sub>n</sub>=1000 or 2000 g/mol were used as macrodiols. Diisocyanates of 1,6-hexamethylene (HDI) or 2,4-toluene (TDI) were employed for chain extension, Fig. 1. The reaction temperature was selected at 50°C or 80°C with molar ratio of macrodiol : diisocyanate at 1:0.5 or 1:0.3. Chain extension progress was investigated by FTIR and titrimetry, measuring the NCO group concentration. Viscosity, chemical and thermal properties of the obtained prepolymers were analysed using vibrational viscometry, FTIR, DSC and other methods. HTPU viscosities increased with decreasing isocyanate groups until their final depletion. HTPU prepolymers, which were synthesized from PCL, showed higher viscosity, compared to those from PEG. They might constitute an OH-component, which could be crosslinked into PU adhesives or plastics for other applications.

## Acknowledgment

This study was carried out under project TERMINUS, funded by the European Union under Horizon 2020. Call: H2020-NMBP-ST-IND-2018. Grant Agreement: 814400.

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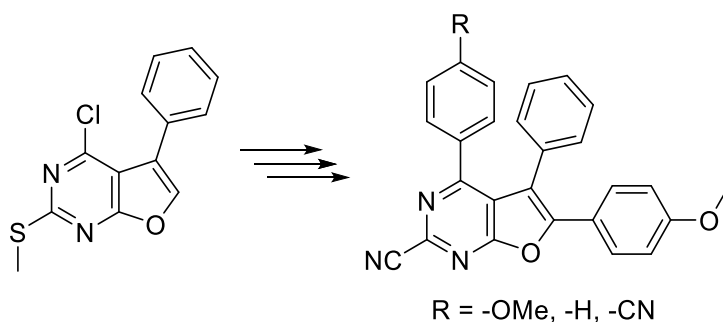


**SYNTHESIS OF 4-ARYL-2-CYANO-6-(4-METHOXYPHENYL)-5-PHENYLFURO[2,3-*d*]PYRIMIDINES VIA Pd(0) CATALYSED REACTIONS. STUDY ON PHOTOPHYSICAL PROPERTIES OF NON-LINEAR HETEROCYCLIC COMPOUNDS**

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Pyrimidine is a strong  $\pi$ -deficient aromatic heterocycle, which can be used as an electron-withdrawing moiety in “push-pull” aromatic systems alongside electron donating groups giving rise to internal charge transfer (ICT). These compounds attracted much attention due to their potential applications in a variety of fields such as nonlinear optics, liquid crystals and OLEDs. Herein, we report on the synthesis and photophysical properties of some furo[2,3-*d*]pyrimidines.



We applied a well-known Suzuki-Miyaura cross-coupling reaction to introduce aromatics with various electronic effects on to the 4<sup>th</sup> position in 2-cyano-4-chloro-6-(4-methoxyphenyl)-5-phenylfuro[2,3-*d*]pyrimidine, which was synthesised in couple of steps from the 4-chloro-2-methylthio-5-phenylfuro[2,3-*d*]pyrimidine. Photophysical data were collected in order to analyse the effect of electronically different substituents on fluorescence.

**Acknowledgements:** this work is a part of ongoing program “Synthesis and functionalization of fused pyrimidine heterocycles, study on heterocyclization reactions” (2015-2020).

# INDOLE CARBOXYLIC ACIDS AS STARTING POINT TOWARDS HETEROARYL INDOLES

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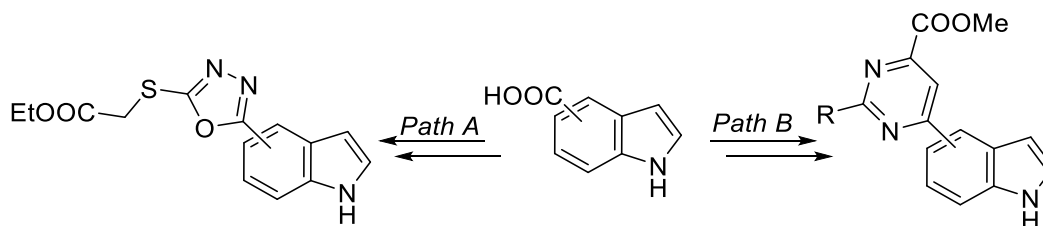
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It is now widely acknowledged that the success of compounds through the drug discovery process is strongly associated with molecular and physical properties. In 2012, Nadin et al. challenged the synthetic community with the task of developing synthetic methodology that would be better suited to the preparation of lead-like molecules [1]. Over the past decade, peptide drugs have been receiving increasing attention from scientists because they often prove to be a preferred alternative to small molecule drugs. In order to overcome inherent weaknesses of peptide drugs and seek increased therapeutic activity, synthetic amino acids are used in peptide drug discovery.

In the present work preparation of heteroaryl indole with carboxylic acid functional group will be presented. Two different pathways were applied to get the desired products.

Path A involved hydrazine synthesis followed by cycloaddition of carbon disulfide. The intermediate was further S-alkylated to give desired indoles with ethyl 2-((5-methyl-1,3,4-oxadiazol-2-yl)thio)acetate functional unit.



Path B involved conversion of indole carboxylic acids to the  $\beta$ -ketoesters. The obtained dicarbonyl compounds were treated with DMF-DMA and amidines to afford the corresponding indoles with methyl pyrimidine-4-carboxylate structural unit.

The structures of the isolated compounds were proved by means of mass spectrometry, IR and NMR spectroscopy.

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# SYNTHESIS AND INVESTIGATION OF BIPOLAR 1, 8-NAPHTHALIMIDE-BASED COMPOUNDS

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Organic materials exhibiting thermally activated delayed fluorescence (TADF) have attracted much attention due to their good performance in organic light emitting diodes (OLEDs) which is possible due to harvesting of triplet excitons. TADF occurs due to reverse intersystem crossing. It is possible when the energy difference between excited singlet ( $S_1$ ) and triplet ( $T_1$ ) energy levels is very low [1]. External quantum efficiencies (EQEs) of TADF OLEDs have been rapidly boosting in past few years [2]. So far, considerable progress has been achieved in EQEs of blue and green TADF OLEDs. In contrast, the development of high-efficiency orange-to-red TADF OLEDs with electroluminescence peak wavelength longer than 580 nm remains far behind. Up to now, there are only few reports of relatively efficient orange-red TADF emitters [3]. For example, orange-red TADF emitter, based on triphenylamine units and heptazine core enabled to achieve EQE of 17.5% with an emission peak of 610 nm [4]. However, the highest EQEs of orange-red TADF OLEDs are significantly lower compared to those of blue and green TADF OLEDs. Consequently, new efficient orange-red TADF emitters are highly demanded to fill the gap. The slow development of efficient orange-to-red TADF emitters is associated with numerous strict molecular design requirements and corresponding difficulties.

With the aim to obtain orange-red emitters for OLEDs, in this work we synthesized bipolar compounds containing 1,8-naphthalimide fragments linked to donor moieties such as phenoxazine, phenothiazine and acridine. The glass transition temperatures of the synthesized compounds were observed in the range of 51-94°C. The optical and photoelectrical properties of the synthesized materials were also investigated. Emission maxima of the solid films of naphthalimide-based compounds were observed in the range of 632-693 nm (Fig. 1).

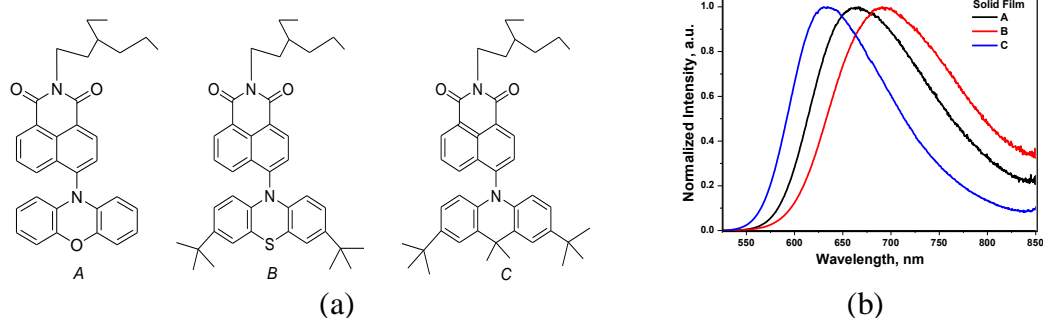


Fig. 1. (a) Structures (A, B, C); (b) fluorescence spectra of solid films of naphthalimide derivatives

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## (9,10-DIOXOANTHRACEN-1-YL)HYDRAZONES WITH AMIDOXIME MOIETY

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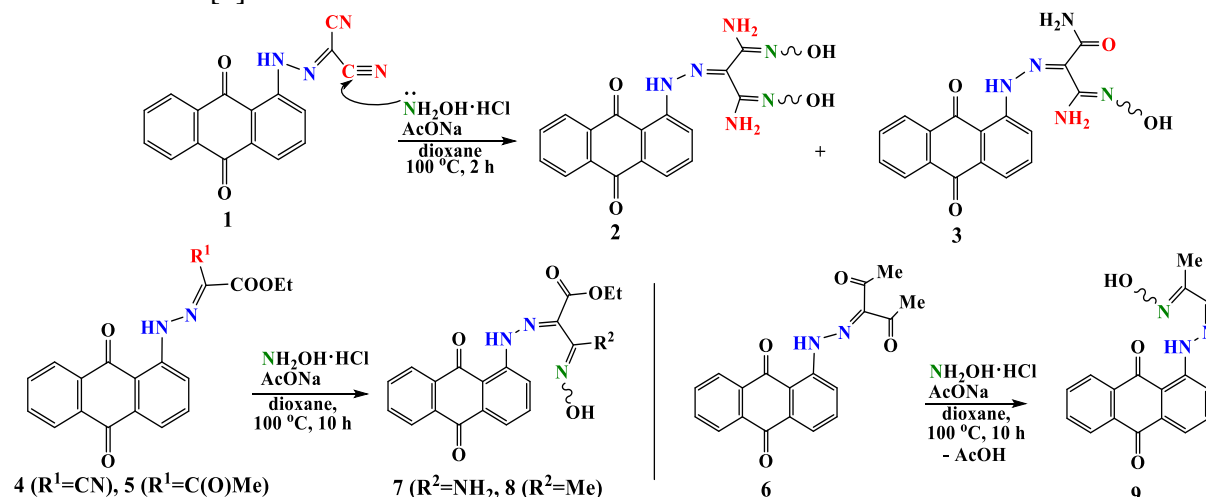
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Amidoxime compounds are valuable objects for organic and medicinal chemistry due to the presence of hydroxyimino and amino functions at one carbon atom. They are widely used as "building blocks" in the synthesis of various heterocyclic systems [1], as selective reagents for the determination of cations of toxic metals and for the development of metalloprotein inhibitors and prodrugs with different types of biological activities [2].

New (9,10-dioxoanthracen-1-yl)hydrazones containing amidoxime fragments were synthesized by the interaction of corresponding hydrazones of malonodinitrile, ethyl cyanoacetate, ethyl acetoacetate, and acetylacetone [3, 4] with hydroxylamine in boiling dioxane in the presence of sodium acetate [5].



It was established that the reaction of N-(9,10-dioxo-9,10-dihydroanthracen-1-yl)carbonohydrazonoyldicyanide (**1**) with NH<sub>2</sub>OH (1 : 2.2, control of TLC, eluent – benzene : acetonitrile) leads to the formation of 2-(2-(9,10-dioxo-9,10-dihydroanthracen-1-yl)hydrazinylidene)-N<sup>1</sup>,N<sup>3</sup>-dihydroxymalonimidamide (**2**) as the major product, and 3-amino-2-(2-(9,10-dioxo-9,10-dihydroanthracen-1-yl)hydrazinylidene)-3-(hydroxyimino)propanamide (**3**) as a minor product. The interaction of hydrazones **4-6** with NH<sub>2</sub>OH (1:1) leads to the formation of amidoximes **7** and **8**. The <sup>1</sup>H, <sup>13</sup>C NMR and LC-MS data showed that the reaction of 9,10-dioxoanthracenylhydrazone **6** with hydroxylamine is accompanied with the elimination of the acetyl fragment formed 1-[2-(2-(hydroxyimino)propylidene)hydrazinyl]anthracene-9,10-dione (**9**). It was determined based on the results of <sup>1</sup>H, <sup>13</sup>C NMR and LC-MS spectra, that the obtained amidoxime compounds exist as one geometric isomer.

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# UPCONVERSION LANTHANIDE-DOPED NaYF<sub>4</sub> NANOCRYSTALS COATED WITH SILICA SHELL

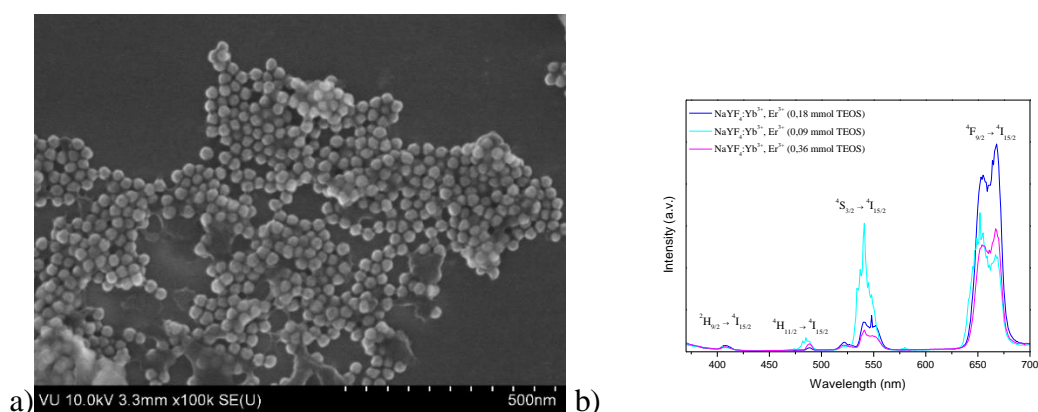
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Organic dyes, fluorescent proteins and quantum dots have been used widely for biolabeling and tissue imaging, but their emerged toxicity and other drawbacks have led to the search of alternative fluorescent probes. Upconverting nanoparticles, which are excited by IR rays to emit visible light, have garnered much attention. They are superior to dyes used previously due to their deep tissue penetration, chemical stability, low cellular toxicity and intense, high resolution images without the need of UV ray excitation [1-3]. Here we demonstrate the synthesis and characterization of water dispersible erbium and ytterbium doped upconverting NaYF<sub>4</sub> nanoparticles.

In order to find out upconversion emission dependence on surface properties the lanthanide-doped upconverting NaYF<sub>4</sub> nanoparticles with different functional groups on surface were synthesized. In this research  $\alpha$ - and  $\beta$ -phase NaYF<sub>4</sub> upconverting nanoparticles doped with Yb<sup>3+</sup> (20%) and various concentrations of Er<sup>3+</sup> (0÷5%) were synthesized via thermal decomposition method at 300-330°C in oleic acid and 1-octadecene. Upconverting nanoparticles were modified via Stöber or microemulsion methods using NaYF<sub>4</sub>:Yb<sup>3+</sup> (20%), Er<sup>3+</sup> (2%), tetraethyl orthosilicate (TEOS) or/and (3-aminopropyl)triethoxysilane (APTES), ammonia and cyclohexane. Synthesized materials were characterized by X-Ray powder diffraction (XRD), scanning electron microscopy (SEM), upconversion luminescence properties were measured with Edinburgh Instruments FLS980 (980 nm excitation) spectrophotometer.



1. Fig. a) SEM image of NaYF<sub>4</sub>:Yb<sup>3+</sup>(20%), Er<sup>3+</sup>(2%) nanostructures, b) luminescence spectra after surface modification using microemulsion method and different TEOS concentration (under 980 nm excitation).

**Acknowledgments:** This research was funded by a grant SINALAN (No. S-LU-18-13) from the Research Council of Lithuania.

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## CONTROLLING UPCONVERSION EMISSION OUTCOME IN Yb<sup>3+</sup>/Er<sup>3+</sup> SYSTEMS

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Due to their unique property of two NIR photon absorption followed by sequential energy transfer to Ln ions, upconverting nanoparticles (UCNP) generate visible emission. UCNP have been recently playing an important role in biomedicine outweighing other luminescent probes such as organic dyes and quantum dots. High signal-to-noise ratio, deeper NIR penetration depth into tissue and low autofluorescence are the main advantages over conventional fluorophores. One of the main goals is to broaden the possibilities of the applications of upconverting materials by being able to improve emission intensity and tune UC emission in various systems. It can be achieved by designing core/shell nanoparticles, varying concentration of dopants and incorporating additional ions into matrices [1].

In this study, NaGdF<sub>4</sub>:20% Yb, 2% Er nanoparticles were additionally doped with alkali (K<sup>+</sup>) ions and transition metal (Cr<sup>3+</sup>) ions. XRD measurements revealed that doping up to 40% of K<sup>+</sup> instead of Na<sup>+</sup> and 50% of Cr<sup>3+</sup> replacing Gd<sup>3+</sup> no additional phase was formed. In case of K<sup>+</sup>, further doping caused formation of cubic phase (or mixture of phases) instead of previously synthesized hexagonal phase nanoparticles. Successful doping into NaGdF<sub>4</sub> was confirmed by the shift of XRD patterns comparing to samples of undoped NaGdF<sub>4</sub> nanoparticles. Although the position of dopant ions and their role is slightly different, luminescent properties were affected in both cases. The R/G ratio of integrated emission increases resulting in shift towards red region under  $\lambda_{exc}=980$  nm irradiation when dopant concentrations are increased. Luminescence lifetime measurements were performed in order to investigate the impact on luminescent properties. Temperature dependent measurements of NaGdF<sub>4</sub>: (20%) Yb, (2%) Er nanoparticles with various doping (K<sup>+</sup> and Cr<sup>3+</sup>) concentrations were carried out. It turned out that the relative emission intensity from the <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>F<sub>9/2</sub> levels (Er<sup>3+</sup>) increase with increasing temperature in the range of 77-500 K. Values of energy distance between <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> levels of Er<sup>3+</sup> were calculated and compared. Optimal values for doping K<sup>+</sup> and Cr<sup>3+</sup> ions will be discussed and proposed.

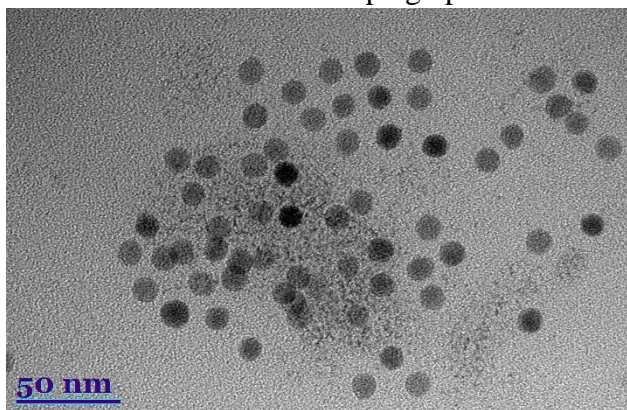


Fig. 1 TEM image of NaGd<sub>0.78</sub>.

**Acknowledgments:** This research was funded by a grant SINALAN (No. S-LU-18-13) from the Research Council of Lithuania.

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## ALGAE AND ASH AS PLANT FOOD IN GRANULATED FERTILIZERS

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With the intensification of agriculture, good nutrient uptake requires not only quality fertilizers but also soil-enriched biofertilizers [1, 2]. This experiment provides data obtained by granulating fertilizers that consist from bioactive component *Chlorella Vulgaris* algae (ChVA) and buckwheat hull ash (BShA). Laboratory drum granulator-dryer was used in the work. It has been found that these materials have a low plasticity and agglomeration process is ineffective if only water was used. Using different concentrations (10, 20 and 30 %) of polyvinyl acetate solutions (PVAS) and of molasses solutions (MS) as a binder improves the quality of agglomeration and granular product (Fig. 1 a and b).

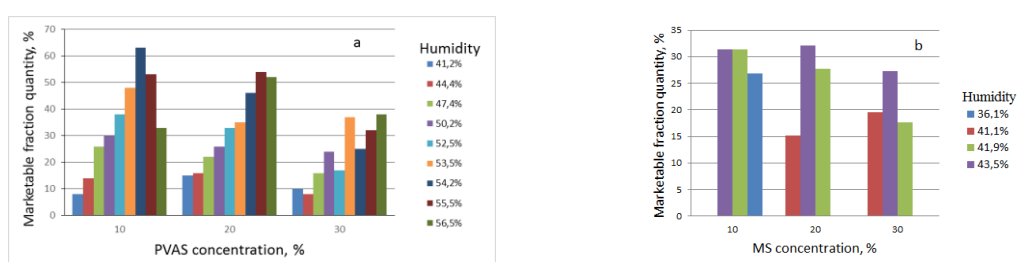


Fig. 1. Quantity of marketable fraction by granulating: a – BShA with PVAS; b – ChVA with MS

However, the results do not meet the requirements for fertilizers. Therefore, mixtures of these raw materials (algae and ash) were granulated. A certain amount (20, 40, 60 %) of the technological recycle (particle size less 2 mm) was also used to improve the quality of the granular product (Fig. 2). Analyzing the results, it was determined that certain conditions (raw material mixture containing 70 % ash and 30 % algae, 20 % molasses solution, 60 % recycle quantity in the mixture), the main characteristics of granular product (granulometric composition and granule strength) meet minimum fertilizer quality requirements (Fig. 3).

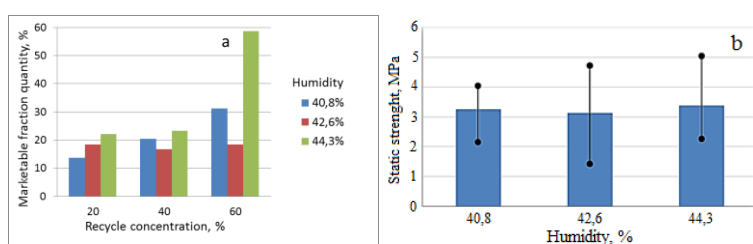


Fig. 2. Granular product marketable fraction parameters: a – quantity, b – static strength using 20 % MS



Fig.3. 0-4-13 fertilizers

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# INVESTIGATION OF SYNTHESIS AND ANTI-MITOTIC ACTIVITY OF NOVEL 2H-PYRAZOLO[4,3-*c*]PYRIDINES

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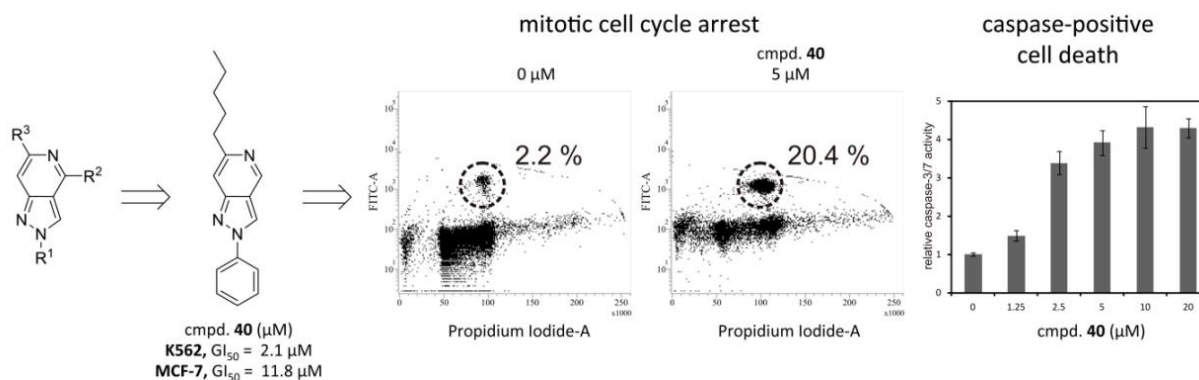
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**Summary:** Organic heterocyclic compounds possessing pyrazole ring attract significant interest due to their various biological and pharmacological activities. In a series of recent publications, we have demonstrated that pyrazole-4-carbaldehydes, carrying an alkynyl function adjacent to the formyl moiety, are valuable starting materials for the construction of condensed pyrazole derivatives. The aim of this study was to synthesize 2H-pyrazolo[4,3-*c*]pyridines, primarily varying by the substituents at the 2-, 4- and 6-positions. Sonogashira-type cross-coupling reaction was employed to yield 3-alkynyl-1H-pyrazole-4-carbaldehydes, ethanones and propanones from the corresponding 1H-pyrazol-3-yl trifluoromethanesulfonates. Subsequent treatment of the coupling products with dry ammonia afforded a versatile library of 2H-pyrazolo[4,3-*c*]pyridines. Newly prepared 2H-pyrazolo[4,3-*c*]pyridines were evaluated for their cytotoxicity against K562 and MCF-7 cancer cell lines. The most potent compounds displayed low micromolar GI<sub>50</sub> values in both cell lines.[1]



**Fig. 1** Biological activity of the lead compound 40

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# LUMINESCENCE OF Eu(II) DOPED AND Dy(III) CODOPED SrAl<sub>4</sub>O<sub>7</sub>

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Strontium aluminate SrAl<sub>4</sub>O<sub>7</sub> structure is monoclinic with space group C2/c (No. 15) and having cell parameters a=13.04, b=9.01, c=5.55 and β=106.502° [1]. It also has high-pressure form called β-SrAl<sub>4</sub>O<sub>7</sub> [2]. Compared to other strontium aluminates (i.e. SrAl<sub>2</sub>O<sub>4</sub>, Sr<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>, SrAl<sub>12</sub>O<sub>19</sub> and Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>), it has less information published in scientific literature. Capron and Douy described synthesis of SrAl<sub>4</sub>O<sub>7</sub> from a spray-dried amorphous precursor, and specified its stability domains [3]. SrAl<sub>4</sub>O<sub>7</sub> has the elemental composition close to that of Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub> and the formation of latter is favored at the detriment of SrAl<sub>4</sub>O<sub>7</sub>. Research showed that kinetics of formation is very low and thus crystallization of SrAl<sub>4</sub>O<sub>7</sub> is sensitive to the heating rate [3].

The current study aims on expanding the knowledge related to strontium aluminates in perspective of persistent phosphors. The goal of this research was to prepare phase pure SrAl<sub>4</sub>O<sub>7</sub> and to investigate its luminescent properties when strontium aluminate is doped with europium and codoped with dysprosium.

During this work, a series of europium doped and dysprosium codoped SrAl<sub>4</sub>O<sub>7</sub> samples were prepared using conventional solid-state synthesis method. Obtained powder materials were characterized using X-ray diffraction analysis and data was analyzed using structural refinement method to determine crystal structure properties, such as unit cell parameters. Luminescence measurements were carried out to record excitation and emission spectra.

## Acknowledgement

This research is funded by the European Social Fund under the No 09.3.3-LMT-K-712 “Development of Competences of Scientists, other Researchers and Students through Practical Research Activities” measure.

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# INVESTIGATION OF SYNTHETIC PATHWAY OF VARIOUS 2-(3-SUBSTITUTED PROP-2-YNYLTHIO) IMIDAZOLES *via* ELECTROPHILIC CYCLIZATION REACTIONS

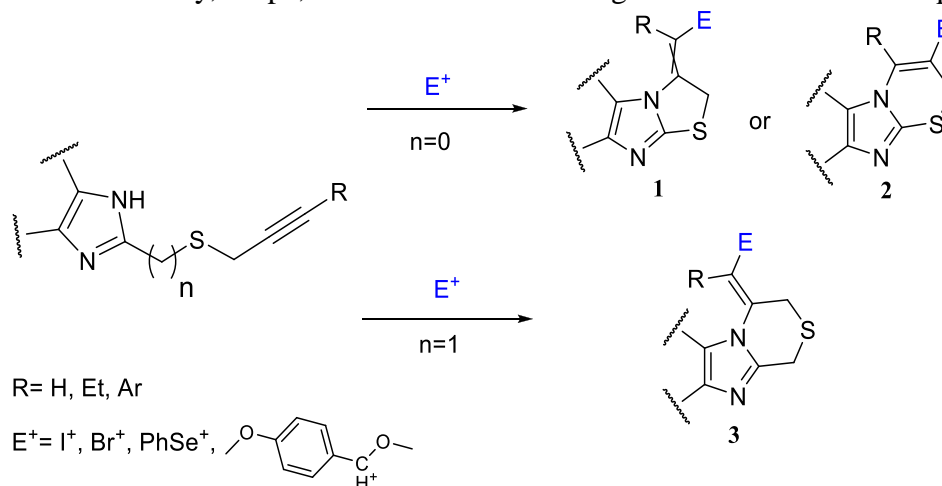
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Imidazo[2,1-b][1,3]thiazine (**2**) and imidazo[2,1-c][1,4]thiazine (**3**) fragments are found in compounds which exhibit potential pharmaceutical properties as tumor cell growth inhibitors, cytotoxic [1], cardiotoxic [2] or antibacterial [3] agents. One of the new routes to imidazothiazine compounds could be through electrophile initiated heteroatom cyclization reaction of alkynes which is used in synthesis of other types of heterocycles [4]. Thus we present the new way to synthesize imidazothiazine ring system *via* electrophilic cyclization of propargylic substrates. This synthetic route also enables variation of substituents in thiazine ring and possible halogen substitution in the system.

For our study 2-(3-substituted prop-2-ynylthio)benzimidazoles were chosen as model reactants in investigation of electrophile induced cyclization reactions. It was found that, cyclization of 2-(prop-2-ynylthio)benzimidazole (R= H) went through 5-*exo*-dig path (**1**) with selected electrophiles. While, 2-(3-substituted prop-2-ynylthio)benzimidazoles (R= Et, Ar) induced 6-*endo*-dig cyclization (**2**) and products were isolated in good yields. Some synthesized compounds **2** were chosen for further modification. However, cyclization of 2-(3-substituted prop-2-ynylthio)methylbenzimidazoles (n=1) resulted only in 6-*exo*-dig intramolecular cyclization (**3**) and in lower yields, as it appears due to the more labile sulphur. More details about reaction selectivity, scope, limitations and used reagents will be discussed in presentation.



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# INFLUENCE OF CALCINED MICA CLAY ON SULFATE ATTACK OF CEMENT STONE

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Additives in cementitious systems have an influence on the durability of cement stone. In order to reduce the deterioration reactions (especially at sulfate attack) of cement stone, various pozzolana additives can be used [1-3]. Calcined clay is one of the earliest known pozzolanic materials and this material allows replacing a part of cement in concrete to improve long-term strength and durability [4, 5]. There is a lack of knowledge about influence of calcined mica clay on sulfate attack of cement stone.

The main aim of this research is to explore the influence of calcined mica clay on the sulfate attack of Portland cement.

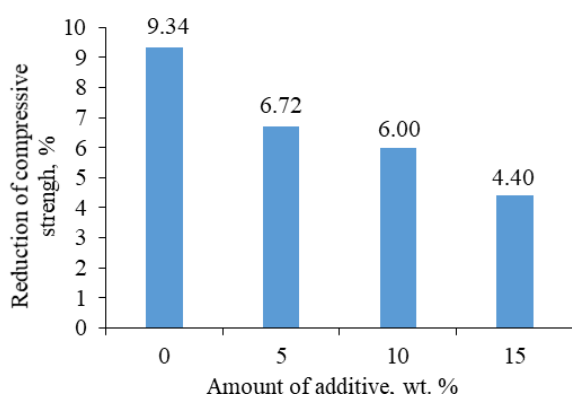
The chemical composition and characteristics of the mica clay taken from an industrial quarry and Portland cement are shown in Table 1.

**Table 1.** Chemical Composition and Characteristics of Raw Materials

Components	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	Loss on ignition	Specific surface area, m <sup>2</sup> /kg
Clay (wt.%)	46.40	14.20	9.40	10.3	4.15	3.03	0.16	0.06	11.46	290
OPC (wt.%)	19.52	5.03	3.05	61.39	3.93	1.06	0.12	2.5	-	350

Samples (30×30×30 mm) were formed from OPC paste with 0, 5, 10, and 15 wt.% calcined at 900 °C mica clay (CMC) additive. After 28 days of hydration in water, samples were transferred to a 5% sodium sulfate solution and stored there for 3, 6 and 9 months.

The results of compressive strength of samples showed that the CMC additive positively affects the resistance of the cement stone to the sulfate attack: after 9 months of curing in the sulfate environment, the samples with 5-15 wt.% CMC additive (97.2–98.8 MPa) exhibited higher compressive strength than the OPC samples without CMC (92.3 MPa).



The most remarkable results to emerge from the data are the compressive strength decrease level (reduction of compressive strength) of the samples treated from 6 till 9 month in the sulfate environment (Figure 1). This data highlighted that after 6 and 9 months of maintenance in a 5% Na<sub>2</sub>SO<sub>4</sub> solution, the compressive strength of OPC samples decreased by 9.34%; whereas, up to 6.72% reduction of compressive strength was fixed in the in the samples with 5-15 wt.% CMC additive.

Figure 1. CMC additive effect on the compressive strength decrease level of the samples treated from 6 till 9 month in the 5 % Na<sub>2</sub>SO<sub>4</sub> solution.

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## VANILLIN-BASED PHOTORESINS FOR OPTICAL 3D PRINTING

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Photopolymerization is the rapid formation of cross-linked polymers from monomers under the influence of the light. Photopolymerization can be initiated by UV-, visible- and rarely by IR-light [1]. 3D printing, also known as additive manufacturing, is a growing technology which has drawn an increasing attention globally and makes a revolutionary impact on products fabrication in areas like medicine, food industry, textile, architecture, and construction [2]. In stereolithography, one of 3D printing technology, resin can be cured by UV light to create 2D patterned layers. By repeating this procedure 3D structure can be created layer by layer [3]. In the last years vanillin and its derivatives are starting to be used in polymer synthesis as their aromatic resin provides high rigidity and thermal stability of resulting polymers [4].

In this study, the cross-linked polymers were obtained by photopolymerization of vanillin diacrylate or vanillin dimethacrylate with 1,3-benzenedithiol using ethyl (2,4,6-trimethylbenzoyl) phenyl phosphinate as photoinitiator. The chemical structure of the photocross-linked polymers was confirmed by IR spectroscopy. The yield of the insoluble fraction of the photocross-linked polymers obtained after Soxhlet extraction with acetone for 24 h was in the range of (87-95) %. Thermal and mechanical properties of vanillin diacrylate- and vanillin dimethacrylate-based photocross-linked polymer films were investigated and compared.

Photorheometry was used to monitor the evolution of thiol-ene photocross-linking process. The UV/Vis real time photorheometry curing tests were performed on a MCR302 rheometer from Anton Paar equipped with the plate/plate measuring system. The most rigid cross-linked polymers were obtained using vanillin diacrylate and ethyl (2,4,6-trimethylbenzoyl) phenyl phosphinate as photoinitiator. In all cases less rigid cross-linked polymers were obtained when vanillin dimethacrylate was used.

It was established by differential scanning calorimetry that the photocross-linked polymers of vanillin diacrylate and vanillin dimethacrylate were amorphous materials with the glass transition temperature of around -5 °C. Their thermal degradation temperatures at the weight loss of 10 %, determined by thermogravimetric analysis, were in the range of 240-270 °C.

Mechanical testing of the photocross-linked polymers was performed by tensile test on a BDO-FB0.5TH (Zwick/Roell) testing machine. The mechanical characteristics of obtained vanillin diacrylate and vanillin dimethacrylate-based photocross-linked polymer films were following: tensile strength was 5-25 MPa, the elongation at break was 0.5-31%, the Young modulus was in the range of 16-2953 MPa.

It was determined that vanillin diacrylate-based photocross-linked polymer films were more rigid and mechanically stronger, whereas vanillin dimethacrylate-based photocross-linked polymer films were more soft and flexible.

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## ONE-STEP PHOSPHOR IN GLASS SYNTHESIS AND CHARACTERIZATION

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As a solid-state lighting source, LEDs have been phasing-out incandescent and fluorescent lamps since the improvement of blue LEDs and white LED commercialization in 1996 [1]. Currently to produce white light, blue LEDs are combined with a yellow YAG:Ce<sup>3+</sup> phosphor which is dispersed in silicone or other organic resin. However, to use them in high brightness applications, high current densities are needed to generate high intensity emission in LEDs. Past a certain point, the amount of generated light drops due to so called efficiency droop phenomena [2]. To circumvent the need for increased current densities, a larger amount of LEDs are used instead. As the junction temperature increases, currently used silicone suffers from color shifting, and luminous efficiency degradation with prolonged use [3]. One of the means to improve thermal conductivity of phosphor plates, allowing higher LED operating temperature range, is to disperse phosphors in glass, ceramic or glass-ceramic matrices [4].

In this work phosphate glasses with different compositions were synthesized. The glass precursors and luminescent materials were ground and mixed together, melted in muffle furnace: molten liquid was poured into premade molds and heated again at lower temperatures to relieve thermal stress. As obtained samples were polished and characterized by x-ray diffractometry, photoluminescence measurements and inductively coupled plasma optical emission spectrometry.

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## GdPO<sub>4</sub>/Eu/Yb-Tm BASED PHOSPHOR SYNTHESIS AND ANALYSIS

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Over the last couple of decades, biocompatible multifunctional magnetic and luminescent nanoparticles have received a lot of attention. Due to their possible applications in magnetic resonance and luminescent imaging, as possible drug carriers etc [1]. Most of these inorganic nanoparticles are rare-earth based materials due to their excellent magnetic and optical properties. Also, some of them are good host materials for dopant ions. One such material is GdPO<sub>4</sub> because of the phosphate groups on its surface that make it biocompatible and stable [2]. Gd<sup>3+</sup> ions have 7 unpaired 4f electrons resulting strong paramagnetic properties. Thus, the samples containing Gd<sup>3+</sup> ions are potential candidates for magnetic resonance imaging. Further gadolinium phosphate can be easily doped with other rare earth elements to make it a luminescent material as well. Europium is commonly used as a dopant because of its long decay times, narrow emission bands and orange-red light emission [3]. Other elements or even a combination of several dopants can be also used to make an upconverting system [4]. However, the particles for bio applications have to be smaller than 100 nm in size, not agglomerated, and must be stable and have high luminescence intensity. Ions from the compounds must not leech into the organism. The small size of particles usually leads to low luminescence intensity but it can be increased by forming a core-shell system [5]. Also, GdPO<sub>4</sub> particles of different size, shape and even of several crystal structures can be prepared. All of these factors influence the stability, as well as magnetic and luminescence properties. They can also affect the toxicity of the compound to the cells. For this reason, a lot of research is still required.

In this work, rare-earth doped gadolinium phosphate was prepared using citric acid assisted hydrothermal synthesis. Effects of synthesis conditions and dopants were investigated. X-ray diffraction analysis was used to determine thermal stability and purity of obtained samples. Scanning electron microscopy and transmission electron microscopy were used to determine the shape and size of particles. Luminescence measurements of particles and their solutions were performed. Thermal gravimetric measurements were used in order to find the amount in the crystal hydrate.

**Acknowledgements.** This research is funded by the European Social Fund under the No 09.3.3-LMT K- 712 “Development of Competences of Scientists, other Researchers and Students through Practical Research Activities” measure.

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# PREPARATION AND CHARACTERIZATION OF STARCH-PLASTIC BLENDS

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Starch is the most common renewable raw material used in production of bioplastics. However, starch alone is hardly useable as a packaging material mainly due to its poor mechanical properties (e.g. brittleness) and its hydrophilic nature. Starch is often modified mechanically, physically or chemically and/or combined with plasticizers or polymeric additives.

Polyethylene (PE) is one of the major sources of commodity thermoplastics used as the matrix in development of biocomposite materials which are extensively used for both nonstructural and structural applications, due to the low cost, recyclability and processing advantages as compared to synthetic composites [1]. PLA (polylactide) belongs to a family of biodegradable thermoplastic polyesters made from renewable resources which is nowadays seen as one of the most promising polymers for commercial use as a substitute for polyethylene [2].

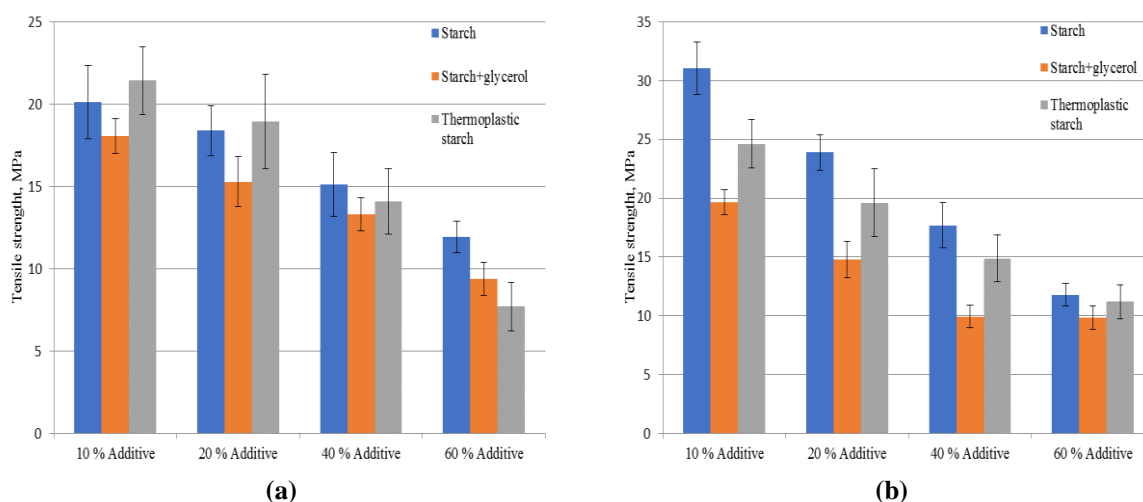


Fig. 1. Ultimate tensile strength of PE/additive (a) and PLA/additive (b) composites

In this work, twin screw extruder was used to blend polyethylene or polylactide with one of three additives: native starch granules, native starch granules mixed with glycerol (mass ratio starch:glycerol 7:3), pre-extruded starch and glycerol mixture - thermoplastic starch (mass ratio starch:glycerol 7:3). Ultimate tensile strength of prepared injection molded samples is shown in figure 1. The results showed that PE composites had lower ultimate tensile strength compared to PLA composites. Also, by increasing the amount of additives, composites with lower ultimate tensile strength are obtained. By comparing different additives one can observe, that lowest ultimate tensile strength was obtained in the case where a mixture of starch granules and glycerol was used. The conclusion can be made, that a mixture of starch and glycerol should be pre-extruded before blending with other polymer matrices, in order to obtain composites with satisfactory ultimate tensile strength.

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# INVESTIGATION OF $\text{Cu}_x\text{S}$ LAYERS ON POLYAMIDE SURFACE BY SEM AND XRD

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Polyamide (PA) as semi-hydrophilic, flexible polymer, which is capable to absorb ions or molecules of various electrolytes from aqueous and non-aqueous solutions.  $\text{Cu}_x\text{S}$  modified polymers are used as conductive substrates for deposition of metals and semiconductors, gas sensors functioning at temperatures close to room temperature, polarizers of infrared radiation, and active absorbents of radio waves [1].

In this work, we report the preparation of electrically conductive  $\text{Cu}_x\text{S}$  layers on polyamide (500  $\mu\text{m}$  thickness) by the chemical bath deposition (CDB) method with the use of  $\text{Na}_2\text{S}_2\text{O}_3$  solution as the sulfurization agent. Deposition of the  $\text{Cu}_x\text{S}$  thin films was carried out at room temperature by using mixture of 0.05 M  $\text{CuCl}_2$  and 0.05 M  $\text{Na}_2\text{S}_2\text{O}_3$  solutions for 16 h [2, 3]. The deposition process was carried out by repeating such deposition cycles 3 times. The films were annealed at 80°C for 30 minutes in air atmosphere. The samples were investigated by XRD and SEM methods after each formation cycle and after annealing.

The results of X-ray structural analysis have shown that geerite,  $\text{Cu}_8\text{S}_5$ , formed after the first and second CDB cycles, and additionally chalcocite,  $\text{Cu}_2\text{S}$ , and copper sulfide,  $\text{Cu}_{1.81}\text{S}$ , phases appeared on the PA surface after the third cycle.

Fig. shows cross-section images of  $\text{Cu}_x\text{S}/\text{PA}$  composite formed by three CBD cycles. It can be seen that continuous surface morphology has formed on the coated surfaces. It has been observed that the annealed  $\text{Cu}_x\text{S}$  films had a finer and homogeneous distribution (Fig. b) than non-annealed  $\text{CuS}$  films (Fig. a).

Electrical sheet resistivity of composite surface at room temperature decreased from 10  $\text{k}\Omega/\square$  after 1<sup>st</sup> cycle to 0.1  $\text{k}\Omega/\square$  after 3<sup>rd</sup> cycle; films with such resistance may find applications as electrical contacts in optoelectronic device structures.

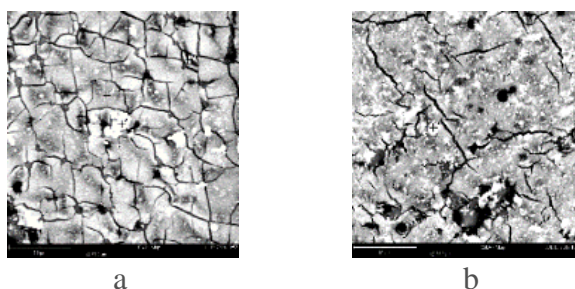


Fig. Surface SEM image of composite formed by 3 CBD cycles (a), and this composite after thermal treatment (b)

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# SYNTHESIS AND STUDIES OF TETRASUBSTITUTED CARBAZOLE COMPOUNDS

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Carbazoles are prevalent as structural motifs in various synthetic materials. As is well known, the properties of carbazole derivatives are closely related to their molecular structures [1]. In the previous papers, the derivatives of carbazole unit as central core were commonly prepared by functionalizing at its 3,6- [2], 2,7- [3] or 9- [4] positions. The as-prepared compounds with thermally and morphologically stable properties can expand the application of carbazole in organic light-emitting devices (OLEDs). Due to their thermal stability, good film-forming properties and high luminescence, the starburst molecules have attracted much more attention to the application in OLEDs, photovoltaics and field effect transistors [5].

In this study, we report a carbazole derivative by using carbazole as the central core and functionalizing at its 1,3,6,8-positions with ethenylaryl moieties and investigation of their thermal, optical, photophysical and electrochemical properties of the synthesized compounds. The synthesized compounds exhibit thermal stability with 5% weight loss temperature exceeding 412 °C. The ionization potential, electron affinity values were estimated by cyclic voltammetry. The analysis revealed that compound with 2-ethenyl-naphthalenyl substituents exhibited higher thermal stability than compounds with 1-ethenyl-2,3,4,5,6-pentafluorophenyl and 4-ethenylpyridinyl moieties. The synthesized compounds form glasses with glass transition temperatures of 59-134 °C. The dilute solutions of the synthesized derivatives exhibit absorption maxima in the range of 355-380 nm, and fluorescence intensity maxima in the range of 400-470 nm. The ionization potential values of the synthesized materials range from 5.27 to 5.58 eV.

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# Hybrid Phospholipid Bilayer surface properties investigation and modification using Scanning Electrochemical Microscopy

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An important component of biological cells is its membrane, which separates the cell from the environment and regulates the exchange of substances inside the cell and vice versa.<sup>1</sup> Since cell membranes are complex systems, models are developed to replicate their properties. One of the widely investigated and modified membrane properties is selective permeability, which can be increased by creating adjustable size pores.<sup>1,2</sup> Scanning Electrochemical Microscopy (SECM) is a fast-growing technology in biological research in which signal is Faradaic current of the tip - ultramicroelectrode (UME). Whereas the size of the UME used vary from few nm to 25  $\mu\text{m}$ , measurements for very small samples with high resolution data are possible.<sup>3</sup> Using SECM different operation it becomes possible with only one instrument investigate the surface properties of the membrane, modify it, and detect changes.<sup>3,4</sup>

In this work a glass plate coated with a layer of tin oxide doped with fluorine atoms (FTO) was used as a substrate for self-assembled monolayer (SAM) and phospholipid bilayer membrane (BLM) formation. A mixture of octadecyl trichloro silane (OTS) and vinyltrimethoxy silane (VTS) was used to form SAM. The hybrid phospholipid bilayer membrane was prepared using the vesicle fusion method from 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) and cholesterol in molar % ratio 6:4 in phosphate buffer solution (PBS) containing 0.1M NaCl, 0.01M  $\text{NaH}_2\text{PO}_4$ , pH 4.6.<sup>5</sup>

Electrochemical measurements were carried out using three electrode system where platinum UME ( $\varnothing$  25  $\mu\text{m}$ ) was used as working electrode, platinum wire as counter and Ag/AgCl/KCl sat as reference. Surface investigation measurements were performed with scanning electrochemical microscope using a feedback mode. Carrying out many targeted approach curve experiments on surface, SECM is used to locally detect membrane defects and the effect of toxin. Characteristic feedback curves of clean, unmodified FTO glass surface was compared to curves of (i) SAM-modified FTO; (ii) a phospholipid membrane-coated FTO prior to interaction with the toxin phospholipase and (iii) a phospholipid membrane-coated FTO after phospholipase interaction with the phospholipid membrane.

BLM electroporation was performed by applying a 1 V voltage to the working electrode for 1.5 minute at a distance of 5  $\mu\text{m}$  from the surface. Approach curves before and after electroporation were compared to detect changes of surface. Since the surface of membrane is more or less heterogeneous, it has been observed that at different points, the electroporation phenomenon with discussed conditions ensues differently.

Whereas different size of tip may be used in scanning electrochemical microscopy there is a great chance that adjustable size of pores may be obtained. Moreover, measurements can be held in a bio-compatible environment. This leads to a promising expectation that SECM has a great potential in investigation of both biological cell membranes and their models.

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# IDENTIFICATION AND REDUCTION OF MICROBIOLOGICAL CONTAMINANTS IN HERBS

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Herbs and their products are widely used in the food, food supplements and pharmaceutical industries worldwide, so it is very important to ensure the quality and safety of raw materials and products. Depending on the external factors, various contaminants are found on the final plant material. This work emphasizes precisely the biological pollution that it is impossible to see with the naked eye. Bacteria, and their spores, molds, yeasts, viruses and other microorganisms on the plant, can complicate storage and quality assurance of raw materials. [1,2] The microbiological contamination of plants is inevitable, and therefore the permissible rates of non-pathogenic organisms are determined according to the nature of the use of herbs. However, the use of plants that have a tolerable amount of bacteria or mold has the potential to affect herbal product users with weaker immunity.

Moulds are widespread natural pollutants in the atmosphere. Researchers mention that leaves and other parts of the plant above the soil have high mould contamination. It is moulds and fungi that are potential allergens and manufacturers of mycotoxins. These chemicals are cancerogenic and quite stable and remain after the mould or fungus death. [3,4] Some types of moulds or bacteria on herbals are antibiotic resistant and can cause infections. [5]

The destruction of microbiology is a major challenge, as different microorganisms can survive under different conditions, and the chemical composition of the plant must be taken into account, without compromising the active components. Ethylene oxide was used to reduce contamination, but was banned in 1989. Gamma radiation is one of the alternatives to pollutants, but it is not fully investigated as to the quality of herbs. [6] In our research we tried other alternative methods – electroporation and cold plasma disinfection. The latter one is highly promising due to it is a nonthermal method that likely would reduce biological contamination of herbs without extreme chemical composition change. [7]

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# ANTIMICROBIAL ACTIVITY OF SOME *LACTOBACILLUS* STRAINS AGAINST PATHOGENS

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In the last century, antibiotics had revolutionized many industries as effective antibacterial drug against bacterial diseases. However, the increased application of antibiotics led to the problem of the development of bacterial antibiotic resistance over time. This requires the necessity of the search of alternative agents without harmful effects. As an option, supplementing probiotics gained interest in recent years [1]. *Lactobacilli* are the major type of lactic acid bacteria (LAB), which have been shown to act as a preservative as well as a probiotic agent [2]. For expanding the possibilities of the application of LAB in the production of new bioproducts for factory farming, it is important to evaluate the antimicrobial activity spectrum of the LAB.

The aim of this study was to evaluate antibacterial activity of LAB strains, previously isolated from rye and wheat sourdough against pathogenic bacterium belonging to *Salmonella*, *Escherichia*, *Staphylococcus* and *Bacillus* genera. Fourteen strains belonging to *Lactobacillus* genus and fourteen new LAB isolates, isolated from three different sourdoughs previously made from wholemeal rye and wheat flours were tested for antimicrobial activity.

The antimicrobial activity of LAB metabolites (supernatants), supernatants that was neutralized to pH 6.5 (for bacteriocin like inhibitory substances analyse BLIS), LAB cells and intracellular metabolites were evaluated using agar well diffusion assay method. Antimicrobial activity was expressed by measuring the inhibition zones diameter (mm) after cultivation of pathogens on Plate count agar medium for 24 hours [3].

Supernatants of tested LAB strains effectively inhibited the growth of gram positive and gram negative bacteria (the diameters of the inhibition zones varied from 10±0 to 35.0±2.3 mm). The highest activity was observed of LAB isolates R1 and R4 against *Staphylococcus aureus* B2 (the diameters of the inhibition zones were 35 and 30 mm, respectively). In summary, the results can be proposed that antimicrobial activity of LAB metabolites strongly depended on LAB strain. The results suggest that the strains isolated from sourdough and belonging to *Lactobacillus* genus could be useful for the production of antibacterial agents against humans and animals diseases.

The research was funded by a grant (01.2.1-MITA-T-852 Inostartas) from Agency for Science, Innovation and Technology (MITA) of Lithuania.

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# PREPARATION AND CHARACTERISATION OF BIODEGRADABLE POLYESTER FILMS

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Non-biodegradable plastic materials are often used for food and beverage packaging, boxes, packaging films, disposable bags and tableware, etc. Most of those plastics are made of fossil fuel which is not renewable and contribute to climate change. One of the solutions to many of today's toughest plastic related problems is to use bio-based and biodegradable polymers for plastic production. They can be mainly classified as agro-polymers (starch, protein, etc.) and biodegradable polyesters (polyhydroxyalkanoates, poly (lactic acid), etc.). These latter, also called biopolyesters, can be synthesized from fossil resources, but main products are obtained from renewable materials. Unfortunately, for certain applications, biopolyesters cannot be fully competitive with conventional thermoplastics due to their weak properties [1]. One of the drawbacks which limits their application is brittleness. Some of the ways to improve the properties of bioplastics are blending them with other polymers or blending them with various additives, such as plasticizers.

Therefore, the aim of this work was to investigate and compare mechanical properties of films prepared from (poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), poly(lactic acid) (PLA), poly(butylene succinate) (PBS)) and their blends. Also, bioplastic films plasticized with triacetin (TRI), polyethylene glycol (PEG) and triethyl citrate (CIT)) were prepared and their mechanical properties were investigated and compared. As could be seen from Fig. 1, highest elongation at break has been when low molecular weight CIT and TRI plasticizers were used. Non-plasticized blends of polymers did not show an increase in elongation at break when compared with films composed of one type of polymer.

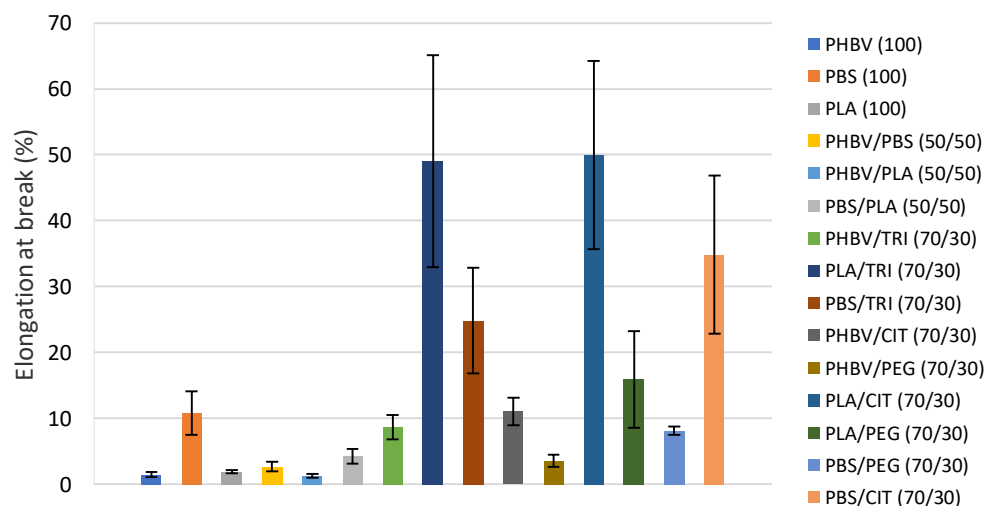


Fig. 1. Elongation at the brake of films composed of neat bioplastic, plasticized bioplastic and blends of bioplastics

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## CARBONATION OF $\alpha$ -C<sub>2</sub>SH AND ITS CALCINATION PRODUCTS

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The reduction of CO<sub>2</sub> emission is a great challenge for the industry of binding materials as, during the production of ordinary Portland cement (OPC), ~5 % of all man-made CO<sub>2</sub> is emitted. Alite is a major mineral in OPC. Another component, belite is considered to be environmentally friendly, because the energy necessary to produce it is equal to 1350 kJ/kg, whereas alite requires approximately 1810 kJ/kg [1]. Due to this difference, 15–20 % of energy consumption is decreased during production. Also, the mentioned process require a smaller amount of CaCO<sub>3</sub>, resulting in reduced amounts of CO<sub>2</sub>. The known synthesis technologies of anhydrous calcium silicates are expensive and complex, because a solid-state sintering requires a high synthesis temperature (1100–1450 °C); sol–gel method involves not only a high calcination temperature (1000–1250 °C), but also very pure initial materials should be used; hydrothermal synthesis of  $\alpha$ -C<sub>2</sub>SH is followed by thermal activation at 600–1100 °C temperature. The latter method is the most advanced and presented in several USA patents [2]. However, the thermal activation temperature is still high and, in comparison with C<sub>3</sub>S, the obtained products have a lower hydraulic activity. For this reason, in this work pressed the wet samples were carried in CO<sub>2</sub> atmosphere. During the mentioned process, CaCO<sub>3</sub> formed in the cement stone and the density, durability and strength of products increased, while the porosity – decreased [3].

The objective of this work was to create an environmentally friendly technology for obtaining nano–sized calcium silicates which will combine hydrothermal synthesis of precursors and their activation at low temperature. Hydrothermal synthesis was carried out at 200 °C for 16 h from burned limestone and opoka mixture with molar ratio CaO/SiO<sub>2</sub> = 2.0. The main product of this synthesis was  $\alpha$ -C<sub>2</sub>SH with small amount of quartz and portlandite. The thermal activation of obtained product and milled its mixture with standard sand (1:1) was carried out at 450 °C and 800 °C temperature. The samples, where water to cement ratio was 0.25, were pressed in a hydraulic press to form 36×36 mm cylinders. After the compaction, the samples were directly transported to the reactor. Mortar samples were treated in the pressure reactor with gaseous CO<sub>2</sub> at 15 bar at 45 °C for 24 h. CO<sub>2</sub> treatment had a positive influence on the sample hardening process – all samples gained a fairly high strength during a relatively short time (Table 1).

**Table 1.** Compressive strength of mortar samples

Material	$\alpha$ -C <sub>2</sub> SH	$\alpha$ -C <sub>2</sub> SH	$\alpha$ -C <sub>2</sub> SH	$\alpha$ -C <sub>2</sub> SH with sand	$\alpha$ -C <sub>2</sub> SH with sand
Calcination temperature, °C	–	450	800	–	450
Compressive strength, MPa	25	21	16	22	20

To our knowledge there were not presented in the literature data, that  $\alpha$ -C<sub>2</sub>SH used like binder material differently anhydrous calcium silicates. The study showed that  $\alpha$ -C<sub>2</sub>SH as a binder material is suitable for carbonation curing and could be used to produce carbonated construction materials. It is very attractive from economic point of view – avoids the high energy consumption that the calcination process requires.

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## SYNTHESIS AND BIOLOGICAL ACTIVITY OF

### 2,4,6,7-TETRASUBSTITUTED-2H-PYRAZOLO[4,3-c]PYRIDINES

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Pyrazole is a common structural unit in many pharmaceuticals and a central axis of numerous ongoing studies devoted to the synthesis and biological evaluation of novel pyrazole moiety-bearing molecules. Annelated pyrazoles are of particular interest as they constitute the core of several well-known drugs, including Sildenafil, Zaleplon and Allopurinol. Among the vast variety of up to now developed biologically active annelated pyrazole derivatives, synthetically demanding 2H-pyrazolo[4,3-c]pyridines are, however, relatively understudied.

Herein we present synthesis, biological activity and optical properties of novel 2,4,6,7-tetrasubstituted-2H-pyrazolo[4,3-c]pyridine derivatives easily accessible from pyrazolidin-3-one. The newly synthesized compounds were evaluated for their cytotoxicity against two human cancer cell lines: K562 (chronic myeloid leukemia cells) and MCF-7 (breast cancer cells). In general, most tested compounds exhibited moderate cytotoxicity, with GI<sub>50</sub> values in the micromolar range.

# SYNTHESIS OF TUNGSTEN OXIDE THIN FILMS AND INVESTIGATION OF GAS SENSING PROPERTIES

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Nanostructured materials are considered as good candidates for gas sensing applications due to their large surface area-to-volume ratio and the size effect. Tungsten trioxide (WO<sub>3</sub>) is a typical n-type semiconductor material with a band gap of 2.5–2.8 eV. It has received much interest for applications in photocatalysis, electrochromic devices, solar energy conversion and gas sensors due to excellent catalytic, optical and dielectric properties, good physical and chemical stability [1]. Gas sensors based on tungsten (VI) oxide are sensitive to a variety of gases such as NO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub> and organic vapours. NO<sub>x</sub> is one of the major toxic pollutants in air, which causes respiratory diseases such as bronchitis, emphysema and heart diseases. In particular, tungsten oxide showed superior sensitivity and selectivity in detecting NO<sub>2</sub> gas [2].

In this work tungsten oxide thin films (WO<sub>3</sub>) were synthesized on glass substrate using sol-gel approach with different additives and annealing temperatures. Firstly peroxytungsten acid (PTA) was synthesized as precursors using sodium tungstate dihydrate (Na<sub>2</sub>WO<sub>4</sub> × 2H<sub>2</sub>O), nitric acid (HNO<sub>3</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Synthesized PTA powder was dissolved in water and ethanol solution and white color sol-gel solution was obtained. Another group of samples was prepared by the same synthesis scheme adding 4% oxalic acid to final sol-gel. Third group of samples was prepared adding PEG 300. After coating procedure samples were annealed at 500 °C, 400 °C and 300 °C for 2 h with heating rate of 5 °C/min. The coatings were characterized using X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) and gas sensing properties were analyzed in gas chamber.

XRD results showed that crystallinity of phases depends on annealing temperature. After annealing at 300 °C crystallinity of tungsten oxide is very low. However after annealing at 400 °C and 500 °C crystalline phases of tungsten oxide were obtained.

Morphology of coatings was analyzed using SEM. It was found to depend on additives and also annealing temperature. 200-400 nm sized particles were observed in the coating synthesized using PTA+EtOH sol-gel. Coating synthesized with oxalic acid looks porous with 1 μm agglomerates. Coatings with PEG look smooth and without pores.

Gas sensing properties were analyzed using different gases (volatile organic compounds, NO<sub>2</sub> and H<sub>2</sub>S). Obtained results depend on many factors including annealing temperatures, different additives and also measurement factors.

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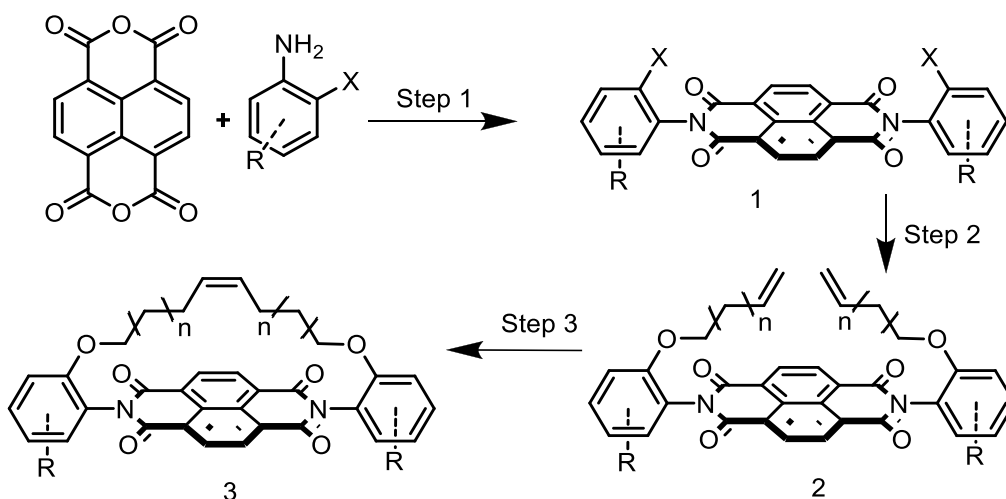
# SYNTHESIS OF NDI MODEL COMPOUNDS POSSESSING STRAPPED – ALKENE MOIETY TO EXAMINE ARYL – ALKENE $\pi - \pi$ INTERACTION

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Derivatives, that contain naphthalene diimide (NDI) frameworks, are considered to be the strongest organic  $\pi$  - acids. [1] This unique property, together with their characteristic to assemble multilayered structures, make NDI derivatives to be promising materials for bioactivatable cross-linking agents [2],  $\pi$  - acid organocatalysts, anion sensors [3] and new molecular optoelectronic and electronic devices [4]. Our research group synthesized and characterized few symmetric aromatic NDI derivatives that contains cyclic alkene fragments with expectation to explore the highly electron deficient aromatic system of NDIs for the modulation of the electron density of alkene double bonds, located on top of the NDI's  $\pi$  -acidic surface.



The starting NDIs **1** were synthesized from corresponding aniline derivatives and commercially available 1,4,5,8-naphthalenetetracarboxylic dianhydride. Experiments were carried out under various conditions to obtain desired products. Lately, phenols were modified to alkoxy groups that contain alkene fragments. Obtained derivatives **2** were used for olefin metathesis on purpose to synthesize model compound **3**.

Acknowledgment: This research was funded by the Research Council of Lithuania (grant no. S-MIP-17-46).

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# SYNTHESIS OF THERMALLY REDUCED GRAPHENE OXIDE AND ITS APPLICATION FOR UREA BIOSENSOR WITH IMPROVED LONG-TERM STABILITY

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Urea biosensors have been introduced to various fields, such as medicine, food quality control, environmental protection, pharmaceutical and agricultural industry [1, 2]. However, effective biosensor fabrication requires immobilization of selective enzymes, which usually have low stability and short lifespan without immobilization. Therefore, the main goal remains to develop an active, layered material, which would not only have the exceptional electric qualities, but also would let to immobilize certain biocomponents, thus maintaining their stability [3]. One of the promising ways to accomplish such task is to integrate carbon materials, which are characterized by unique mechanical, electrical and thermal properties, into analytical systems [4].

Aiming to create stable urea biosensor, thermally reduced graphene oxide (TRGO) was synthesized. Initially, graphite oxide samples were prepared using Hummers' method and pre-washed 5, 8 and 13 days to reduce the excess of sulphate ions. Then the specimens were reduced using thermal reduction and fractionation equipment. Acquired TRGO fractions were analysed using x-ray diffraction and Brunauer–Emmett–Teller analysis. Activity and stability of the biosensors containing TRGO with different characteristics and urease was investigated. Urea biosensor possessing favourable stability was applied for urea monitoring in industrial technology of fertilizers.

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# THE SYNTHESIS OF BELITE–CALCIUM SULFOALUMINATE CEMENT AND ITS PROPERTIES

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## Introduction

Portland cement is the most widely consumed binder in the world: Every year more than four billion tons of this material were produced [1]. However during production of Portland cement enormous amount of CO<sub>2</sub> are released (5–7% of global emissions, e.g. 0.89-1.1 ton CO<sub>2</sub> from 1 ton Portland cement) and huge amounts of energy are consumed (about 3% of the world's total energy production) [2]. In order to solve mentioned problems, new environmentally friendly binder materials (belite-calcium sulfoaluminate, belite, carbonatable calciumsilicates), which could be used instead of OPC, are in great demand [3]. Thus, the aim of this work was to synthesize belite-calcium sulfoaluminate cement (BCSA) cement by using industrial wastes and to determine its properties.

## Materials and methods

The prepared initial mixture (calcium carbonate – 66.67 %; granite cutting waste – 14.35; aluminum hydroxide – 9.47 %; silica gel waste – 3.81 %; gypsum – 3.17 %; iron (III) oxide – 2.50 %) were placed in a forming cylinder and compressed by a hydraulic presser machine (10 Mpa). The obtained tablets were sintered in four steps in a high temperature furnace, when the selected temperature range varied from 1000 °C to 1250 °C.

## Results

It was determined that optimal synthesis conditions for BCSA clinker is 1100–1150 °C temperature, because raw materials were fully reacted and only hydraulic active compounds (belite, mayenite, ye'elimite, brownmillerite) were formed. Microcalorimetric analysis data showed three exothermic reactions and the total heat release after 72 hours was 264 J/g. The previous results were confirmed by XRD, STA, FT-IR and SEM analysis.

## Acknowledgement

This research was funded by a grants No 09.3.3-LMT-K-712-10-0265 from Research Council of Lithuania.

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# IMMOBILIZATION OF NATURAL BIOACTIVE COMPOUNDS BY CATIONIC OR ANIONIC POLYSACCHARIDES

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**Introduction.** Natural bioactive compounds such as phenolic acids and anthocyanins are denoted by anti-cancer, anti-inflammatory, antioxidant and antibacterial properties. What concerns their active properties, they are widely used in cosmetics, pharmaceuticals and food industry. However, these compounds are unstable, sensitive to heat, oxidation and light, and therefore quickly lose their beneficial properties. The biological activity of these compounds could be preserved by the immobilization into modified natural or synthetic polymers thus creating delivery systems for active components [1-3].

In this work the biological activity of phenolic acids and anthocyanins has been preserved by the immobilization in polysaccharides containing cationic or anionic groups.

**Results and discussion.** Microgranules of phenolic acids/modified starch complexes were obtained by the equilibrium adsorption of caffeic acid (CA), chlorogenic acid (CGA) and rosmarinic acid (RA) onto cationic cross-linked starch (CCS) with degree of substitution of quaternary ammonium groups of 0.42. The adsorption models have been used to describe the equilibrium adsorption data. The Langmuir adsorption model indicated that CA, CGA and RA were adsorbed onto quaternary ammonium groups of CCS. The calculated values of the Dubinin-Radushkevich mean free energy  $E_{DR}$  and Freundlich constant  $n_F$  confirmed the ion-exchange mechanism and favourability of adsorption. Immobilization of phenolic acids onto CCS prevented the rapid loss of antioxidant activity and secured the prolonged radical scavenging activity which could be related to gradual release of CA, CGA and RA from CCS microgranules.

Microgranules of the carrageenan/anthocyanins (CARG/ATC) complex were obtained by adsorption of ATC from the wild bilberry extract onto cross-linked CARG derivatives. Two-variable mathematical adsorption models have been applied to describe the isotherms of equilibrium adsorption: the Langmuir sorption model confirmed electrostatic interaction between the flavylium cations of ATC and the sulfate groups of cross-linked CARG. The values of the Freundlich constant  $n_F$  and the Dubinin–Radushkevich adsorption energy  $E_{DR}$  indicated that ATC adsorption was moderately difficult on cross-linked CARG and physical forces also begin to play a role in the ATC adsorption alongside with the electrostatic interaction between the ATC flavylium cation and the sulfate groups of CARG. Lyophilized microgranules of the cross-linked  $\kappa$ -CARG/ATC complex have been used to prepare a prototype of antioxidant and anti-inflammatory rectal suppositories.

**Conclusions.** The complexes of CA, CGA, RA, ATC and polysaccharides exhibited the prolonged antioxidant activity. Phenolic acids and anthocyanins are effectively released from the microgranules of the complex into the model intestinal and gastric media.

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# CONTROLLABLE SYNTHESIS OF TRICALCIUM PHOSPHATE (TCP) POLYMORPHS BY WET PRECIPITATION: EFFECT OF WASHING PROCEDURE

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Calcium hydroxyapatite (HA),  $\alpha$ -TCP and  $\beta$ -TCP are alloplastic bone substitutes that belong to the class of calcium phosphate ceramics (CPCs). Being injectable, bioactive and biocompatible, CPCs are promising for bone tissue engineering applications and are used as scaffolds and carriers to deliver stem cells, drugs and growth factors [1, 2].  $\alpha$ - and  $\beta$ -TCP have same chemical composition, but due to different structure, density and solubility, more soluble polymorph  $\alpha$ -TCP is used as powder component of various bone cements while  $\beta$ -TCP - as biodegradable bioceramics [3]. It is well known that changing synthesis conditions could lead to final product with aspired structure, morphology or physiochemical properties [4]. The aim of this study was to report on the effect of washing procedure of the as-prepared calcium phosphate precipitates on the synthesis of TCP polymorphs.

$\alpha$ - and  $\beta$ -TCP were synthesized by wet precipitation method using  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and  $(\text{NH}_4)_2\text{HPO}_4$  as starting materials. Calcium to phosphorous molar ratio was kept 1.5. As-prepared precipitates were filtered, washed with distilled water and different volume of specific solution: distilled water, ethanol, isopropanol, acetone and acetonitrile. Washed materials were dried in oven overnight and annealed in the furnace in air.

The crystallinity, crystal structure and structural changes were evaluated by X-ray diffraction (XRD), Fourier-transform infrared (FTIR) and Raman spectroscopy. Thermal behavior of the dried precipitates was investigated by thermogravimetric analysis (TGA). Scanning electron microscopy (SEM) was used for the characterization of morphological features of the synthesized products.

$\alpha$ - and  $\beta$ -TCP polymorphs were prepared by wet precipitation procedure at nearly identical thermal conditions. It was shown that the nature and amount of washing agent determines structure and morphology of the as-precipitated species and formation of TCP polymorphs after the thermal treatment.

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# THE IMPACT OF RAW MEAL COMPOSITION ON LOW-BASE CALCIUM SILICATE HYDRATES SYNTHESIS

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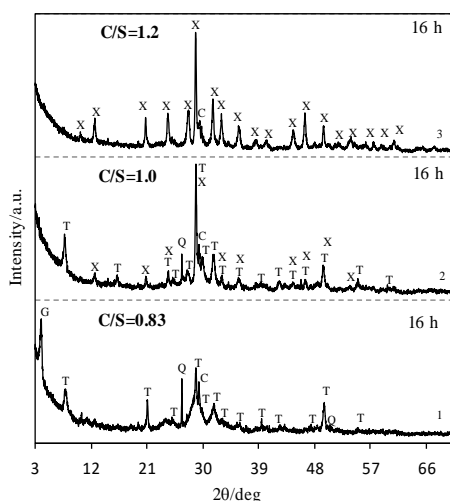
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Compounds formed in a CaO–SiO<sub>2</sub>–H<sub>2</sub>O system are called calcium silicate hydrates and are widely used due to special features and for practical benefit. The main ones, 1.13 nm tobermorite (CaO/SiO<sub>2</sub> =0.83) and xonotlite (CaO/SiO<sub>2</sub> =1.0) are very efficient for heat insulating and fire-resistant material [1]. These compounds are obtained during the hydrothermal synthesis at 180-240 °C usually after long period of curing. The situation is even more complicated when the natural raw materials are used [2]: ions of the impurities have a big influence on the formation and properties of low-base calcium silicate hydrates [3].

One of the suitable materials for the synthesis of calcium silicate hydrates is carbonated opoka – silica-calcite sedimentary rock. The aim of this work was to investigate the influence of the raw meal composition on the intermediary and final compound formation. The products were synthesised in unstirred suspensions from lime-calcined opoka mixtures with molar ratios CaO/SiO<sub>2</sub> =0.83; 1.0 and 1.2 at 220 °C for 4, 8, 12, 16, 24 and 72 h and analysed by XRD and STA methods.

The general tendency is that easy obtained and higher crystallinity 1.13 nm tobermorite and xonotlite are formed not in the mixtures of stoichiometric composition, but in those of which basicity is slightly higher. Consequently, in the mixture with CaO/SiO<sub>2</sub> =0.83, 1.13 nm tobermorite always forms together with low-base calcium silicate hydrate (CaO/SiO<sub>2</sub> = 0.66) gyrolite (Fig. 1, curve 1). In mixture with CaO/SiO<sub>2</sub> =1.0, similar amounts of 1.13 nm tobermorite and xonotlite are formed (Fig. 1, curve 2) and the relationship between them is practically unchanged even after the extension of hydrothermal synthesis duration to 72 h. It should be noted that xonotlite of high crystallinity degree and without impurities of other calcium silicate hydrates is formed only in the mixture with CaO/SiO<sub>2</sub> =1.2 (Fig. 1, curve 3).



**Fig.1.** XRD patterns of the hydrothermal synthesis products after 16 h at 220 °C. Indexes: C–calcite, T–1.13 nm tobermorite, G–gyrolite, X–xonotlite, Q–quartz.

The main reason for this unconventional process of calcium silicate hydrates formation is the impurities in the raw materials (Al<sub>2</sub>O<sub>3</sub> =2.75 %; Fe<sub>2</sub>O<sub>3</sub> =2.36 %; SO<sub>3</sub> =1.11 %, when CaO/SiO<sub>2</sub> =1.0). Al<sup>3+</sup> ions incorporate in the crystal lattice of calcium silicate hydrates by replacing Si<sup>4+</sup> ions. SO<sub>3</sub> binds 3.3 times more CaO into hydroxyllellsteadite Ca<sub>10</sub>(SiO<sub>4</sub>)<sub>3</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>2</sub>. For these reasons, the reactive medium basicity decreases. Therefore, when synthesizing calcium silicate hydrates from natural raw materials it is always necessary to carefully evaluate the influence of impurities on the course of both basic and co-reactions.

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# INFLUENCE OF RAW MEAL COMPOSITION ON SINTERING AND CARBONATION OF CALCIUM SILICATES

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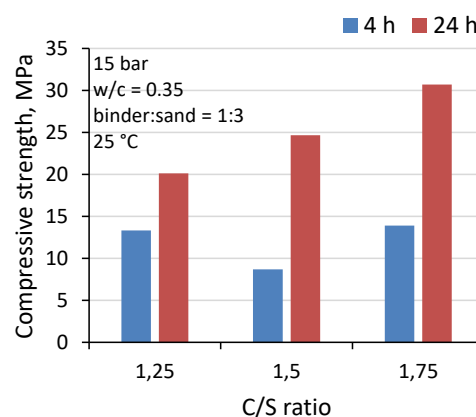
In order to address the ongoing attempt to reduce the adverse effect of the Portland cement manufacture, i.e. CO<sub>2</sub> emissions exceeding 5 % of total global anthropogenic emissions [1], it is important to seek for alternative solutions. One of which is reduction of cement CaO/SiO<sub>2</sub> (C/S) ratio by producing low-lime calcium silicates that not only emit lower amounts of CO<sub>2</sub> in the clinkering process but also hardens in the CO<sub>2</sub> atmosphere thus confining it in the concrete stone. However, the mineral composition of such binders highly rely on their C/S ratio. Thus the main objective of this work was to investigate the C/S ratio influence on the calcium silicate formation that later on could be used for concrete cured in the CO<sub>2</sub> atmosphere.

For this reason, three different raw meal compositions with C/S ratios of 1.25, 1.5 and 1.75 were chosen, in which the desired low-lime calcium silicates are – wollastonite (CaSiO<sub>3</sub> or CS), rankinite (Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> or C<sub>3</sub>S<sub>2</sub>) and larnite (Ca<sub>2</sub>SiO<sub>4</sub> or C<sub>2</sub>S). Table 1 shows the obtained clinker component XRD peak net area based on C/S ratio and calcination temperature.

As can be seen in table 1, the dominant component in mixture with C/S = 1.25 was wollastonite, C/S = 1.5 – rankinite and C/S = 1.75 – larnite. The obtained binders were later on used to determine the compressive strength dependence on the C/S ratio (fig. 1).

**Table 1** Clinker component XRD peak net area dependency on the C/S ratio and calcination temperature

C/S		1000 °C	1100 °C	1200 °C	1250 °C	1275 °C
1.25	CS	3.51	6.034	-	-	-
	C <sub>3</sub> S <sub>2</sub>	-	-	0.867	0.734	0.694
	C <sub>2</sub> S	0.812	1.428	-	-	-
1.5	CS	1.947	2.29	-	-	-
	C <sub>3</sub> S <sub>2</sub>	-	-	-	1.582	1.613
	C <sub>2</sub> S	1.308	1.801	1.012	-	-
1.75	CS	0.978	0.812	-	-	-
	C <sub>3</sub> S <sub>2</sub>	-	-	-	0.842	0.919
	C <sub>2</sub> S	2.015	1.926	1.349	-	-



**Fig. 1** Compressive strength

For determination of compressive strength, the obtained binders were mixed with sand (1:3), moistened (w/c = 0.35) and pressed to form cylindrical samples, that were hardened in the CO<sub>2</sub> atmosphere, using 15 bar pressure, for 4 and 24 h. As can be seen in Fig. 1, while carbonating the samples for 4 h, all of them gained similar compressive strength of 10±3 MPa. While increasing the carbonation duration up to 24 h, strength increased parallel to increase of the C/S ratio and reached 30 MPa with binder of C/S = 1.75.

The obtained results has shown, that mineral composition is directly related to the C/S ratio, while higher C/S ratio binders lead to higher compressive strength.

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# INTRINSIC STRUCTURE-THERMODYNAMICS CORRELATIONS OF FLUORINATED BENZENSULFONAMIDES AS INHIBITORS OF HUMAN CARBONIC ANHYDRASES

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The carbonic anhydrases are established as therapeutic targets. There are 12 catalytically active CA isozymes in human body. At least 30 CA sulfonamide inhibitors have been used as drugs to treat glaucoma, epileptic seizures, altitude sickness, and as diuretics. However, most of them exhibit poor selectivity towards target isozymes and result in various side effects.

In this study a class of 4-substituted-benzensulfonamides and 4-substituted-2,3,5,6-tetrafluorobenzensulfonamides as inhibitors of CA is reported [1]. Isothermal titration calorimetry was used for direct measurement of observed thermodynamic parameters, such as change of Gibbs free energy  $\Delta G$ , enthalpy  $\Delta H$ , and entropy  $\Delta S$ . To confirm enzyme inhibition and binding affinity, stopped-flow  $\text{CO}_2$  hydration and fluorescent thermal shift assays were applied. The combined use of these methods provided a detailed picture of enzyme-inhibitor interactions [2].

Changes in the protonation of enzyme, inhibitor and buffer affect the observed thermodynamic parameters of binding. Each binding reaction should be dissected in order to determine the intrinsic thermodynamic parameters that are independent on experimental conditions. Intrinsic structure-thermodynamics correlations showed that several fluorinated compounds bind selectively to carbonic anhydrase I with strongly exothermic enthalpy and extremely high affinity [3].

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## SYNTHESIS OF NOVEL FUSED PYRAZOLE-AZEPANE DERIVATIVES

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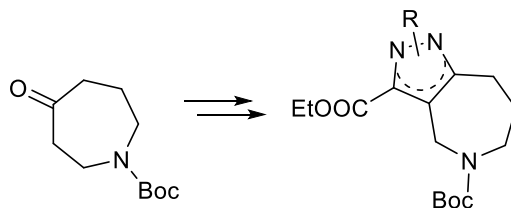
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Pyrazole ring containing molecules often possess interesting biological activities and are thus of significant importance to medicinal chemistry [1, 2] etc. Furthermore, pyrazole moiety containing carboxylic acids have found an application as building blocks in organic synthesis for designing of pharmaceuticals and agrochemicals [3]. On the other hand, fused azepanes have also been identified as privileged motifs in medicinal chemistry [4]. The synthetic combination of the two pharmacologically relevant pyrazole and azepane motifs can provide interesting hybrid building blocks for development of new lead molecules.

The aim of the present work is the synthesis of novel *N*-substituted fused pyrazole-azepane systems. The target compounds were prepared starting from 4-oxoazepane-1-carboxylate *via* keto esters reaction with hydrazine hydrate and subsequent alkylation reaction of pyrazolecarboxylate with various alkylhalides.



The structures of the synthesized new compounds were confirmed by <sup>1</sup>H, <sup>13</sup>C NMR, IR spectroscopy and HRMS spectrometry methods.

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# **Ni FOAM METALIZATION AND INVESTIGATION OF THEIR ELECTROCATALYTIC ACTIVITY TOWARDS ALCOHOL OXIDATION REACTION**

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Metal foams are lightweight cellular materials inspired by nature. Wood, bones and sea sponges are some well-known examples of these types of structures. In fact, solid metallic foams are the conserved image of the corresponding liquid metallic foam. The main applications of metal foams can be grouped into structural and functional, and are based on several excellent properties of the material. Structural applications take advantage of the light-weight and specific mechanical properties of metal foams; functional applications are based on a special functionality, i.e., a large open area in combination with very good thermal or electrical conductivity for heat dissipation or as electrode for batteries, respectively [1].

Ni foam has high purity and porosity of ca. 70-89 %. Ni foam has unique properties, such as exceptional integrity, light weight, high porosity, internal strength, corrosion resistance and good electrical and thermal conductivity. These properties make Ni foam customizable for batteries, light optics, as catalyst for fuel cells or as capacitor material [2-3].

In this work Ni foam was used as a substrate for deposition of Co, Cu and W coatings. The metals mentioned were deposited on the Ni foam surface using electroless and electrochemical deposition methods. The composition and morphology of deposited coatings were characterized by Inductively Coupled Plasma Optical Emission Spectroscopy and Field Emission Scanning Electron Microscopy. The coatings formed were investigated as electrocatalysts towards oxidation of alcohols. The measurements were carried out on the coated Ni foam 1x1 cm electrode in alkaline ethanol, methanol and ethylene glycol solutions by using cycle voltammetry.

It has been determined that electrocatalytic activity of fabricated materials depends on the formation method. It has been found that Co coating deposited on Ni surface by electroless deposition method showed higher electrocatalytic activity if compare with the Co coatings deposited by electrochemical way. The electroless deposited Co showed the highest electrocatalytic activity towards ethanol oxidation reaction, while coating having electrochemically deposited Co showed the highest electrocatalytic activity towards ethylene glycol oxidation reaction.

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# INVESTIGATION OF PROPERTIES OF TRIPHENYLAMINE PHENYLETHENYL DERIVATIVES CONTAINING TERTIARY AMINE GROUPS

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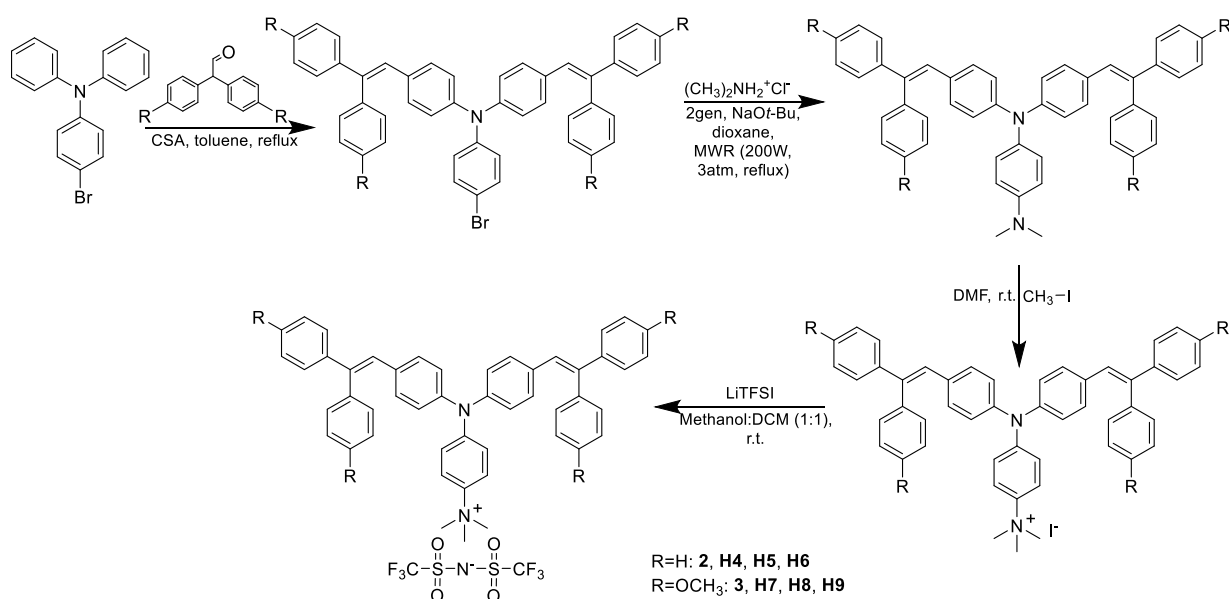
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Triphenylamine (TPA) compounds are versatile charge transport materials, demonstrating high emission efficiency and interesting interactions in solid state. Their spectroscopic emission parameters highly depend on surrounding medium owing to strong CT character in solution. Although TPA compounds demonstrate good charge transport capabilities, further optimization via molecular design is required.

In this work, various TPA molecular systems with varying number of additional dimethylamine and phenylethenyl substituents were thoroughly investigated. Additionally, influence of quaternarization of tertiary amine groups in the triphenylamine backbone on emission and electronic properties was analyzed.



# BIOINSPIRED ADHESION COPOLYMERS CARRYING CATECHOL GROUPS: SYNTHESIS AND PROPERTIES

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It is well established [1] that excellent adherence properties of blue mussels to rocks in wet conditions are predetermined by catechol-containing amino acid, 3,4-dihydroxyphenylalanine. Many catechol group containing polymeric materials were synthesized which were designed to be used as adhesives, anticorrosion polymer coatings, and surface modifiers [2]. Between these polymeric materials, there are only very few examples of the brush copolymers carrying catechol groups [3]. The main task of the present work was to synthesize and study brush copolymers containing PEO side chains and carrying units with catechol groups providing excellent adhesion in aqueous media and lubricating properties to the modified surfaces.

Polymerization of catechol group containing monomers is a challenge since catechol groups act as weak inhibitors of radical reactions, and are readily oxidized to quinones. In order to avoid undesirable reactions, we used two approaches – protection of the catechol group present in a monomer or introduction of moieties with catechol group by modification of random copolymers.

Random brush copolymers were synthesized by RAFT copolymerization of poly(ethylene oxide) methyl ether methacrylate  $M_n$  950 (PEOMEMA) with acetone protected dopamine methacrylamide (A-DOPMA) (the first approach), or PEOMEMA with DMAEMA (the second approach). Copolymerization kinetics and the copolymers were studied by size exclusion chromatography with triple detection (RI, LS, and DP) and  $^1\text{H-NMR}$  spectroscopy. Degree of polymerization of the copolymers was close to 100, and the dispersity index  $\mathcal{D}$  less than 1.2.

The acetone protecting groups of A-DOPMA units in the copolymers were removed using trifluoroacetic acid. DMAEMA units in the copolymers by the second approach were quaternized with 2-chloro-3,4-dihydroxyacetophenone (QDMAEMA). The copolymers of PEOMEMA and DOPMA are catechol groups containing brush copolymers without charge, and the copolymers of PEOMEMA and QDMAEMA are cationic catechol groups containing brush copolymers.

Resistance to oxidation of the catechol copolymers was studied by UV-Vis spectroscopy, and nanoscale wear resistance of the adsorbed layers by AFM-based methodology. The copolymers with protected catechol groups were resistant to UV irradiation, while those with deprotected catechol groups were susceptible to oxidation. The most unstable were cationic catechol groups containing copolymers. The copolymers with catechol groups formed a more wear resistant polymer layer on silica compared to cationic brush copolymers. The combination of cationic and catechol anchoring groups, as in the mussel adhesive proteins, provided the most wear resistant polymer layers.

## ACKNOWLEDGEMENTS:

In collaboration with Prof. Per M. Claesson, KTH, Sweden.

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# VIABILITY OF CASCADING APPLICATION OF POLYAMIDE WASTE INTO LUBRICANT BASESTOCK BY PARTIAL HYDROLYSIS

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Polyamide waste is difficult to recycle in part due to its chemical resistance. In this study, partial hydrolysis of PA10.10 was performed under several types of aggressive environment seeking high yields of a PA10.10 trimer, see Fig. 1, where R=H.

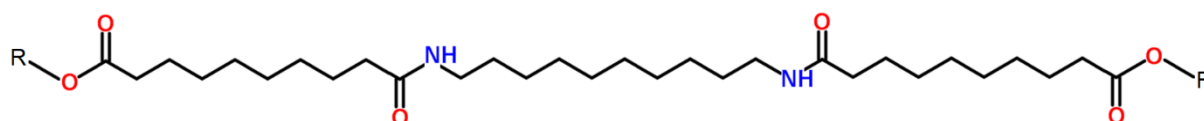


Fig. 1 Structure of the target products: PA10.10 trimer (R=H), basestock (R=C<sub>8</sub>H<sub>17</sub>) and wax (R=CH<sub>3</sub>).

Other polyamides, e.g. PA6.6 (a.k.a. Nylon 6.6), can also be hydrolyzed using the same concept, which involves esterification of the trimer with 2-ethyl hexanol (2EH) in order to produce a basestock for lubricants (R=C<sub>8</sub>H<sub>17</sub>). PA10.10 was selected, since 1,22-di-2EH-docosenedioate had pour point of -57°C [1], so it was reasonable to expect the trimer diester with 2EH (R=C<sub>8</sub>H<sub>17</sub>) to show good fluidity. Two hydrolytic pathways were tested. High pressure hydrolysis of PA10.10 pellets resulted in reduction of the pellet size and increase in surface roughness. Both effects were more pronounced in neutral media, while size reduction was not as evident in basic media. Unfortunately, hydrolysis generated a mix of highly polymeric materials with monomers of diamino decane and sebacic acid. Yields of PA10.10 trimer appeared negligible. The second hydrolysis pathway under ambient pressure in 50% H<sub>2</sub>SO<sub>4</sub> resulted in heavy froth on the surface. After adding 20% acetic a. the froth dissolved, splitting the mix into two phases. Products from the high-pressure pathway were also blended with sulfuric and acetic acids. The pellets which had been partially hydrolyzed in neutral media yielded a dark homogeneous solution, while those of basic media produced two phases.

Concurrently, organic synthesis of the proposed basestock was attempted in order to verify that fluidity and other lubricant properties of the target product (R=C<sub>8</sub>H<sub>17</sub>) were acceptable. Monomethyl sebacate chloride was reacted with diaminodecane at 2:1. But the resulting wax (R=CH<sub>3</sub>) was extremely tough with its melting point at 163°C. Due to very poor solubility in organic solvents transesterification with 2EH could not be performed. Most likely, the trimer is excessively linear and fluidity would be problematic even after the transesterification with 2EH. Molecular architecture should include more branching for viscometric and other lubricant properties to be satisfactory. Therefore, trimers from partial hydrolysis of PA10.10 or larger monomer polyamides cannot be employed for a cascading application into a lubricant basestock. Nevertheless, the monomers such as sebacic acid could be considered for recycling once isolated.

## Acknowledgment

The project COSMOS has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 645405.

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**SYNTHESIS OF NOVEL CONSTRAINED ANALOGUES OF  $\gamma$ -AMINO BUTYRIC  
ACID (GABA) VIA THE Rh(I)-CATALYSED CONJUGATED ADDITION  
REACTION OF ARYLBORONIC ACIDS**

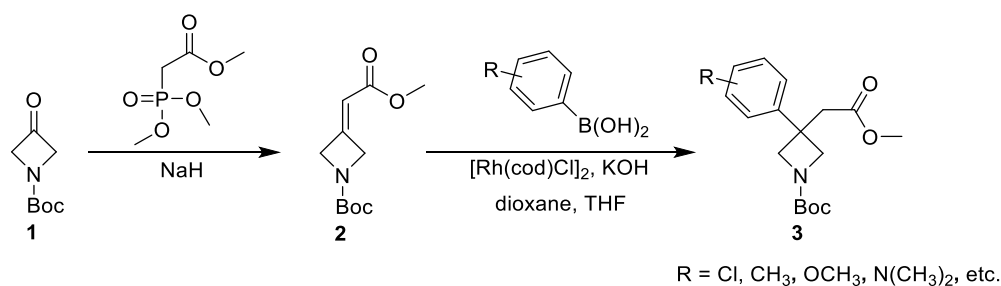
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$\gamma$ -Aminobutyric acid (GABA) is a major inhibitory neurotransmitter in the mammalian central nervous system. It is known that alterations in GABA metabolism have been found to be involved in a number of CNS disorders, including epilepsy, Huntington's chorea, Parkinson's and Alzheimer's disease, anxiety, depression and other [1]. Due to the important role of GABA in organisms, new GABA analogues are continuously being sought in order to develop new biologically active agents.

In the present work novel GABA analogues, possessing the azetidine ring as a carrier of the amine functionality were designed and synthesized. The synthesis started from the preparation of the  $\alpha,\beta$ -unsaturated ester **2** by the condensation of N-Boc-3-azetidinone **1** with trimethylphosphonacetate under the Horner-Wadsworth-Emmons reaction conditions (Fig. 1). After stirring at room temperature for two hours  $\alpha,\beta$ -unsaturated ester **2** with various arylboronic acids in the presence of rhodium(I)-catalyst, the desired conjugate addition adducts **3** were obtained in a good yields [2]. The target amino acid derivatives were prepared as N-Boc protected methyl esters. The structures of the novel compounds were confirmed by <sup>1</sup>H, <sup>13</sup>C NMR, IR, MS, HRMS spectroscopy.



**Fig. 1.** Synthesis of novel methyl (3-arylazetidin-3-yl)acetate derivatives.

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# DEFATTED CRANBERRY POMACE EXTRACT INCREASES SAFETY AND ANTIOXIDANT POTENTIAL OF PORK BURGERS DURING *IN VITRO* GASTROINTESTINAL DIGESTION

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Cranberry pomace is a juice pressing by-product, which is comprised of seeds, skins and stems. Bioactive compounds (polyphenolic antioxidants, antimicrobials), which remain in the pomace are known for their potential in inhibiting several bacteria (*E. coli*, *L. monocytogenes*, etc.); however, the studies on the possibilities of using of cranberry pomace extracts in meat products are still scarce. The aim of this study was to determine antimicrobial activity of cranberry pomace ethanol extract against some spoilage/pathogenic bacteria, to evaluate its effect on various quality characteristics of pork burgers and assess antioxidant potential during *in vitro* digestion of burgers.

Minced pork meat was mixed with appropriate ingredients and divided into 4 batches: without inoculum (RC), with inoculum (RCI), with 2% of extract (RCL), and with 2% of extract and inoculum (RL). The samples RCI and RL were mixed with 1% of the inoculum consisting of four *L. monocytogenes* serotypes at final concentration 10<sup>2</sup> cfu/g (ILSI – 18, ILSI – 29, C170, C3771), *B. thermosphacta* and *P. putida* at final concentration 10<sup>4</sup> cfu/g. Two repetitions of pork burgers were packed under modified atmosphere consisting of 20% CO<sub>2</sub> and 80% N<sub>2</sub>. All samples were stored at 4 °C. Microbial growth of unwanted bacteria, pH, metmyoglobin, color and the changes of thiobarbuturic acid reactive substances (TBARS) of pork burgers were measured during storage. Global antioxidant response (GAR) was measured after *in vitro* oral step, gastric and intestine digestions of freeze-dried samples.

The results showed that higher amount of MetMB was found in RCL burgers than in RC burgers, most likely, due to a lower pH. Therefore its redness (a\*) value was higher than in control samples without any additives, possibly due to the berry extract color. Cranberry pomace extract has an effect on the formation of oxidation product as well: malondialdehyde content was reduced in burgers during their storage. Also, 2% of ethanol extract reduced the growth of *L. monocytogenes*. All freeze-dried samples were subjected to *in vitro* gastrointestinal digestion and antioxidant capacity was measured by different methods (ORAC, ABTS<sup>+</sup>, TPC and e-BQC device) after each digestion phase. Addition of pomace extract increased antioxidant potential of burgers at all digestion phases, oral, gastric and intestine. Consequently, cranberry pomace extract additives may be considered as promising means of increasing meat product's safety and enriching it with functional ingredients, which might provide health benefits.

# NEW (BI)PHENYL SUBSTITUTED 9-(2,2-DIPHENYLVINYL)CARBAZOLES AS HOLE TRANSPORTING MATERIALS FOR EFFICIENT RED PHOLEDs

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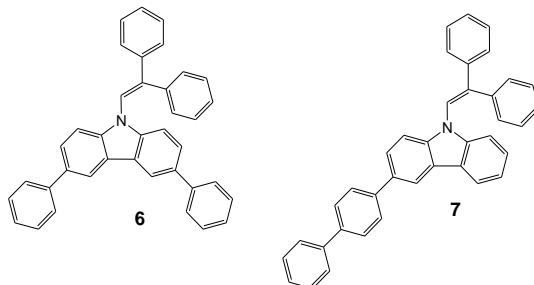
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Phosphorescent organic light emitting diodes (PhOLEDs) have attracted much attention because they use both singlet and triplet excitons for generation of light, making 100% internal quantum efficiency possible. Achieving the high level internal quantum efficiency depends on several factors, including high quantum yield emitters, exothermic energy transfer from host to emitter, effective exciton confinement as well as balanced carrier transport [1]. It is well known that carrier transporting materials are crucial to enable a balance carrier transport from cathode and anode [2]. Considerable exertion is needed for the development of efficient red PhOLED devices, because the lower gap of red phosphors usually induces serious carrier trapping, leading to higher operation voltages and carrier imbalance [3]. Accordingly, it is desirable to exploit new hole transport materials to create red PhOLEDs with reduced power consumption and improved efficiency.

In this study, the new low cost 9-(2,2-diphenylvinyl)carbazole-based derivatives with aryl substitutions were synthesized and investigated. Our previous study found that introducing the diphenylvinyl fragment in carbazole ring could increase spatial hindrance of the moiety and the derivatives could be used for the preparation of thin and stable amorphous layers on substrates [4]. Phenyl or 4-biphenyl substituted 9-(2,2-diphenylvinyl)carbazole based derivatives (6 and 7) are shown below.



We have examined the novel hole transporting materials in the fabrication of red PhOLEDs. The respective peak efficiencies were recorded at 8.7 % (5.6 cd/A and 3.9 lm/W) and at 8.7 % (5.4 cd/A and 3.8 lm/W), correspondingly, for the devices using 3,6-diphenyl-9-(2,2-diphenylvinyl)carbazole (6) and 3-(4-biphenyl)-9-(2,2-diphenylvinyl)carbazole (7) as hole transporting materials. The high efficiencies of the red PhOLEDs suggest great potential of the new (2,2-diphenylvinyl)carbazole based electroactive materials for applications in OLED devices.

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## Acknowledgement

This research was funded by a grant No. S-MIP-17-64 from the Research Council of Lithuania.

# SYNTHESIS OF ISATIN HYDRAZONES AND INVESTIGATION OF THEIR ANTIOXIDANT AND ANTIBACTERIAL ACTIVITY

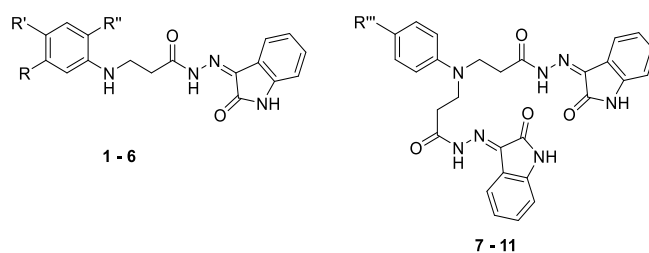
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Recently, hydrazone derivatives have attracted considerable attention in the medicinal chemistry due to their wide range of biological activities, such as antimicrobial, analgetic, anti-inflammatory, etc [1]. Isatin is a heterocyclic compound, which derivatives exhibit numerous biological activities, including antifungal, antiviral, antibacterial, antitubercular, antimalarial, etc [2].

Compounds **1–11** were synthesized by condensation reaction of the corresponding hydrazides with isatin (Scheme).



**1** R = R' = R'' = H; **2** R = H, R' = CH<sub>3</sub>, R'' = H; **3** R = H, R' = OCH<sub>3</sub>, R'' = H; **4** R = H, R' = OC<sub>2</sub>H<sub>5</sub>, R'' = H; **5** R = H, R' = Br, R'' = H; **6** R = NO<sub>2</sub>, R' = H, R'' = CH<sub>3</sub>; **7** R''' = H, **8** R''' = CH<sub>3</sub>; **9** R''' = OCH<sub>3</sub>; **10** R''' = OC<sub>2</sub>H<sub>5</sub>; **11** R''' = Cl.

Scheme. Isatin derivatives **1–11**.

Antioxidant and antibacterial properties of the synthesized compounds **1–11** were screened. 3-((4-Ethoxyphenyl)amino)-N'-(2-oxindolin-3-ylidene)propanehydrazide (**4**) has shown the best DPPH radical scavenging activity (87%). In the reducing power assay, the highest activity was determined for 3-((4-methoxyphenyl)amino)-N'-(2-oxindolin-3-ylidene) propanehydrazide (**3**) and compound **4** with optical density 1.62 and 1.59, respectively. In the ABTS (TEAC) assay, compounds **3** and **4** scavenged the ABTS radical 100% at 58 and 59  $\mu\text{mol/l}$  concentrations, respectively. All synthesized compounds have been identified as good scavengers of hydroxyl radicals with activities from 74.5 to 90.4% in deoxyribose assay.

The majority of compounds exhibited antibacterial activity against the tested bacteria strains. Hydrazides **1–11** were the most active against *X. Campestris*. The inhibition zone of N'-(2-oxindolin-3-ylidene)-3-(p-tolylamino)propanehydrazide (**2**) was 0.9 cm and the one for compound **4** was 0.84 cm. Compounds **2** and **4** inhibited the best growth of the only tested Gram-positive bacteria *B. Subtilis* with inhibition zones 0.68 cm and 0.41 cm, respectively. 3-((4-Bromophenyl)amino)-N'-(2-oxindolin-3-ylidene)propanehydrazide (**5**) was identified as the most active against *E. coli* bacteria (0.75 cm). The SAR analysis has shown that the good antibacterial activity of the synthesized compounds is related to the presence of the methyl (**2**), methoxy (**3**), and ethoxy (**4** and **10**) groups as well as halogen atoms, i.e. bromine and chlorine (**5** and **11**) in their structures.

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# GRANITE DUST – NON-PLASTIC AND FLUXING ADDITIVE FOR BUILDING CERAMICS

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In Lithuania for production of building ceramics together with the main raw material – easy fusible hydromicous clay – non-plastic additives as sand, grog and sawdust most often are used. These additives reduce the drying and firing shrinkage of ceramics, also they reduce drying sensitivity, defects and deformations of the structure during formation process and drying [1]. At this time, companies are looking for new, cheaper additives that will stimulate formation of the melt in a ceramic body at lower firing temperatures.

Granite processing (sawing, polishing, cutting) generates large amounts of waste. Due to very fine granulometry this waste (dust) doesn't find more areas of use, so it usually falls on landfills. The chemical composition indicates that granite dust contains SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, Na<sub>2</sub>O, K<sub>2</sub>O and MgO. In the mineralogical composition of this waste dominate quartz, Na and K plagioclase feldspars, chlorite and mica groups minerals [2, 3]. Both fluxing oxides (Na<sub>2</sub>O and K<sub>2</sub>O) and auxiliary fluxing oxides (Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO), as well as the earlier mentioned feldspars, could improve sintering of ceramic body. The quartz and other non-plastic materials in the composition of granite dust could act as a ceramic mass plasticity reducing additives [4, 5]. Therefore, the purpose of this work was to determine the influence of granite dust additive on the properties of the clay mixture formation mass and on the sintering of the ceramic body and to evaluate the possibilities of using it as a non-plastic and fluxing additive in building ceramics production.

Hydromica, easily fusible clay from Girininkai pit, granite waste from JSC "Granite" and sand (Zatyščiai pit) were used in this research. In order to estimate additive influence on the properties of clay body, 3, 5, 7% and 10% of granite dust were added into the clay. The samples were fired 1h at 1000–1075 °C. It has been found that as the amount of granite dust in the clay mass increases, drying shrinkage decreases from 4 to 12%, firing shrinkage, depending on the firing temperature, increases from 3 to 41%, and water absorption decreases by about 6%. These results show that granite dust is non-plastic and a fluxing additive for ceramics. Therefore the possibility of replacing sand in the clay forming mixture with granite dust was investigated later. The samples with 5, 7 and 10 % of granite dust, 4 % of grog and 3 % of sawdust were formed. It was established that granite dust could be used as sand replacement in forming mixture of building ceramics since forming mass drying and firing shrinkage as well as density and water absorption of the ceramic body varies insignificantly. It should be noted that compression strength of ceramic body with granite dust additive fired at 1000 °C and 1025 °C, is 22 to 37 % (depending on the amount of additive) higher than ceramic body with sand. The obtained results are based on changes in mineral composition as determined by XRD analysis.

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# SOL-GEL SYNTHESIS OF Mg(X)/Al (X = Mn, Co, Ni, Cu, Zn) LAYERED DOUBLE HYDROXIDES

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Layered double hydroxides (LDH) is a class of layered materials based on brucite ( $\text{Mg}(\text{OH})_2$ ) crystal structure. A general chemical formula of the material can be expressed as  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}(\text{A}^{y-})_{x/y}\cdot z\text{H}_2\text{O}$ , where  $\text{M}^{2+}$  (Mg, Zn, Ni, Co, . . .) and  $\text{M}^{3+}$  (Al, Ga, Cr, . . .) are divalent and trivalent metal cations respectively,  $\text{A}^{y-}$  is an intercalated anion which is located in the interlayer spaces along with water molecules.  $\text{A}^{y-}$  compensates the positive charge created by the partial substitution of  $\text{M}^{2+}$  by  $\text{M}^{3+}$  in a positively charged metal hydroxide layers. [1,2].

In present study, the Mg(X)/Al (X=Mn, Co, Ni, Cu, Zn;) compounds were synthesized via aqueous sol-gel method. Their mixed metal oxides were obtained after thermal treatment at 650 °C and subsequently reconstructed in water to layered structure. Synthesized materials were characterized using XRD, SEM, BET and FTIR analysis.

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# SYNTHESIS OF Au NANOPARTICLES WITH SiO<sub>2</sub>, MnO<sub>2</sub>, AND TiO<sub>2</sub> SHELLS FOR SURFACE ENHANCED RAMAN SPECTROSCOPY

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Due to the relatively simple preparation, biocompatibility, optical and electronic properties gold nanoparticles (AuNPs) are widely used for labeling, delivery, imaging and sensing. The plasmonic property of AuNPs allows using them for detection of different analytes by Surface Enhanced Raman Spectroscopy (SERS). However, a direct interaction of research object with bare nanoparticles is the important disadvantage. Inert shells (SiO<sub>2</sub>, MnO<sub>2</sub>, TiO<sub>2</sub>, etc.) perfectly solve this problem, because prevent chemical and electrical contacts among plasmonic cores and probe substrates, analytes and environment. Measurement technique with such particles spread over a surface of analyzed material was firstly published in 2010 and named Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy (SHINERS). Since when SHINERS is being used in surface and biological sciences, semiconductor materials, electrochemistry, food and environment safety etc. [1].

A classic spherical AuNPs were prepared by reduction of auric chloride with sodium citrate by earlier reported example [2]; then three different shells were grown on the colloids; and finally, the core-shell nanoparticles were purified using centrifugation. Three types of synthesized core-shells nanoparticles (Au@SiO<sub>2</sub>, Au@MnO<sub>2</sub>, Au@TiO<sub>2</sub>; Fig. 1) were successfully used for SHINERS experiments with benzenethiol as a model compound. It was shown, that received spectra data can complement each other and it is certainly useful for SHINERS, where comprehensive research of complex structures is required.

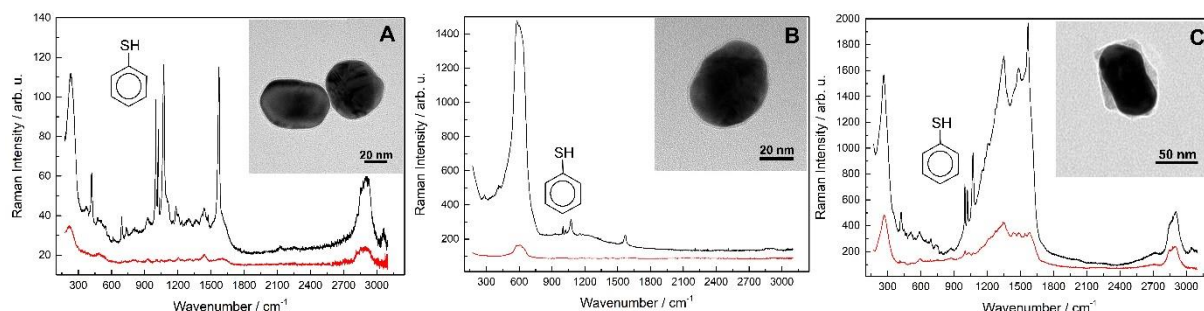


Fig. 1. Raman spectra of Au@SiO<sub>2</sub> (A), Au@MnO<sub>2</sub> (B), and Au@TiO<sub>2</sub> (C) – red lines; SHINERS spectra of benzenethiol with Au@SiO<sub>2</sub> (A), Au@MnO<sub>2</sub> (B), and Au@TiO<sub>2</sub> (C) – black lines. HR-TEM images of Au@SiO<sub>2</sub> (A), Au@MnO<sub>2</sub> (B), and Au@TiO<sub>2</sub> (C) are shown in right corner.

In conclusion, the specific method of Au@TiO<sub>2</sub> synthesis allowed obtain the largest nanoparticles compared to others synthesized AuNPs. We also observed that SHINERS spectrum with Au@SiO<sub>2</sub> has the highest SERS enhancement factor, and SHINERS spectrum with Au@MnO<sub>2</sub> has the least impurities from adsorbed surfactants used for nanoparticle preparation.

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## LOCAL ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY FOR THE EVALUATION OF LABELLED ANTIBODIES

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Electrochemical impedance spectroscopy (EIS) is a powerful, non-destructive and informative technique, which has been successfully applied for the characterization of GOx-based biosensor surfaces [1]. However, conventional EIS based techniques represent only averaged response of the entire electrochemical system. In order to get more advanced mapping of the electrochemical system, scanning electrochemical microscopy (SECM) merged with EIS (SEIM) could be applied. In the SEIM based technique localized impedance measurements could be performed in the frequency range when the surface of interest is scanned by an ultramicroelectrode (UME). The result of SEIM could be visualized by mapping one of the calculated parameters, e.g. charge transfer resistance or double layer capacitance as a function of 3D coordinates [2,3]. The detection of antigen and antibody interaction at the localized surface areas can be performed by SECM [4]. SECM is a better technique than spectroscopy and ellipsometry, which can be used for the determination/evaluation of proteins on the surface but do not indicate or map their exact location.

In this research, SEIM was applied for the experiments on: i) a gold wafer; ii) a gold wafer modified with a self-assembling monolayer (SAM) made of 11-mercaptopundecanoic acid and iii) a gold wafer modified with SAM and enzyme-labelled antibodies. The efficiency of covalent enzyme-labelled antibodies immobilization and location of these conjugates on the surface were evaluated applying the most suitable equivalent electrical circuits (EEC). The thickness and ion-permeability of formed protein layer was evaluated by the calculation of charge transfer resistance ( $R_{CT}$ ) in selected EEC.  $R_{CT}$  increased together with every added modification layer.

### Acknowledgements

This research was funded by the European Social Fund according to the activity “Development of Competences of Scientists, other Researchers and Students through Practical Research Activities” measure No.: 09.3.3.- LMT-K-712- 10-0169.

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## USE OF COAGULATION AND ADSORPTION FOR THE REMOVAL OF SANODURE GREEN DYE BY GROUNDWATER TREATMENT RESIDUALS

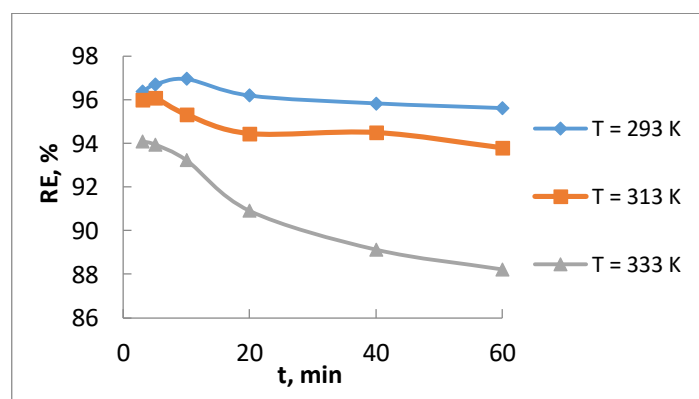
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Sanodure Green LWN anionic azo dye is a commercial product used for dyeing of anodized aluminium. The dye deposited on the surface of aluminium oxide provides the transparent layer that reflects the colour [1]. Colour removal from wastewater is still a major challenge [2]. Several methods including coagulation-flocculation, adsorption, advanced oxidation processes, membrane techniques and biological degradation have been applied for decolourization of wastewater [3, 4]. In this work, a combined process of coagulation-flocculation and adsorption of Sanodure Green LWN dye was studied using groundwater treatment residuals (GWTR). The solid waste with the main component of ferric oxide/hydroxide represents a material with a dual function. During the treatment of wastewater containing Sanodure Green LWN dye, in an acidic medium it can act as coagulant as well as adsorbent. The optimum conditions for the dye removal were studied varying coagulant-adsorbent dosage, contact time and temperature. Factors influencing the decolourization process such as solution pH and dye concentration were also discussed. The dye removal efficiency (RE) increased with decreasing pH values from 6 to 2. Initial dye concentration was varied from 50 to 1000 mg/L to obtain sorption isotherms at 20°C temperature. An increase in temperature from 20 °C to 60 °C produces a negative impact on the removal efficiency of Sanodure Green LWN dye. As shown in Fig. 1, at 20 °C temperature the optimum time for the dye removal efficiency was obtained at 10 min. At higher temperature, it gradually decreases with time. The low cost inherently formed groundwater treatment residuals can be considered as an effective material on removing Sanodure Green LWN dye at short time periods.



**Fig. 1.** Effect of contact time and temperature on the removal efficiency (RE) of the Sanodure Green LWN dye from 100 mg/L solution.

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# CORROSION OF ELECTROLYTIC MANGANESE COATINGS IN 3% NaCl SOLUTION

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Corrosion properties of Mn coatings depend on their mechanical properties and electrodeposition conditions, therefore corrosion potentials of electrolytic Mn coatings deposited on mild steel substrate from the manganese ammonium sulphate bath (MASB) with 2.20 mmol/l Te(VI) additive at different cathodic current density (10–30 A/dm<sup>2</sup>) and temperatures (20–80°C) were measured in naturally aerated 3% aqueous NaCl solution at the initial immersion moment and potential change with time.

Investigation of corrosion of Mn coatings in 3% NaCl medium has led to the conclusion that Mn coatings interfere with Te in a similar manner as Se [1 – 3], and consequently the corrosion resistance of coatings increases in chloride solution.

At the initial moment of the immersion into 3% NaCl solution, the corrosion potentials of Mn coatings deposited from the MASB with 2.20 mmol/l Te(VI) additive at cathode current density 15 A/dm<sup>2</sup> and at temperatures in the range of 20°C–80°C, are very similar and fall into the -1250 – -1300 mV range. During the first day, corrosion potential of Mn coatings deposited from 20 °C MASB increased the most, namely up to -1100 mV, the one of the coating deposited at 40 °C increased very slightly, i.e. up to -1200 mV, while the potential for the coatings deposited from 60 °C and 80 °C MASB remained almost unchanged. During the 2-4 days, potentials of the Mn coatings deposited at 20°C, 40°C and 60°C gradually increased until -1070 mV, -1140mV and -1190 mV, respectively. During the 5–10 days, potentials of the Mn coatings deposited from 20 °C and 40 °C MASB remained stable, whereas the one for the coatings deposited at 60 °C continued to increase. Meanwhile, within 2–10 days potential of Mn coatings deposited at 80 °C increased very slightly up to -1250 mV, but its value remained the lowest.

The calculated corrosion current strengths of Mn coatings has shown that Mn coatings electrodeposited from MASB with 2.20 mM Te (VI) additive at 20°C and 40°C and cathode current density 15 A/dm<sup>2</sup> corroded the fastest at the initial moment of the immersion into a corrosive medium. However, after 1 day corrosion slowed down from 4 to 2 times, whereas after 3–10 days these coatings corroded 2.5–3 times slower than at the moment of initial immersion into the corrosive medium.

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