

# INTERNATIONAL CONFERENCE



Vilnius, Lithuania 2018



# THE INTERNATIONAL CONFERENCE PROCEEDINGS BOOK

OCTOBER 25-27, 2018 VILNIUS, LITHUANIA

# "THE GOOD MAN IS THE FRIEND OF ALL LIVING THINGS." –GANDHI

The international conferences EcoBalt are dedicated to the most recent scientific and technological developments in the field of environmental analysis, environment and its protection, green and sustainable chemistry.

Goals of EcoBalt 2018

The conference will bring forward most recent scientific and technological developments in the field of environmental science, environmental analysis, analytical, green and sustainable chemistry.

The conference will be aimed towards environmental problems – air, water, soil contamination assessment and options for its reduction, new, environmentally friendly products, recycling, and environmental education.

It is a great chance for scientists, industry and students in the Baltic and related regions to come together and share knowledge and discuss issues in relation to our environment. EcoBalt 2018 will be extended with sections on sustainable materials and technologies.



### Scientific Conference Committee:

Arnold Adam (Germany) Andrew R. Barron (United Kingdom) Vadims Bartkevics (Latvia) Aldona Beganskiene (Lithuania) Ewa Bulska (Poland) Edita Garskaite (Lithuania) Koit Herodes (Estonia) Mihkel Kaljurand (Estonia) Viktor Kanicky (Czech Republic) Aivaras Kareiva (Lithuania) Ivo Leito (Estonia) Sanjay Mathur (Germany) Rasa Pauliukaite (Lithuania) Pierre Rabu (France) Milda Radziute (Lithuania) Rimantas Ramanauskas (Lithuania) Egidijus Rimkus (Lithuania) Razak Seidu (Norway) Gunnar Svensson (Sweden) Sigitas Tamulevicius (Lithuania) Eugenijus Valatka (Lithuania) Arturs Vīksna (Latvia)

### Organizers





# **ThermoFisher** S C I E N T I F I C





















**A**Mavis

### **Conference Programme**

### Date: Thursday 25<sup>th</sup> October, 2018

### Venue: Ministry of Environment of the Republic of Lithuania, Jakšto 4/9, Vilnius, 506 hall

8:00-9:00	Registration		
9:00-9:30	Opening ceremony, Session I		
	Chair of the session Prof. Rimantas Ramanauskas		
	Welcome by Prof. Aivaras Kareiva.		
	<ul> <li>Welcome by the Minister of the Environment of the Republic of Lithuania.</li> </ul>		
	Welcome by Vic	e-Rector of Vilnius University	y Prof. Rimantas Jankauskas
9:30-10:20	Prof. Dr. Andrew R.	Ser Cymru Chair of Low	Flexible Approaches to Water Treatment
	Barron	Carbon Energy and	and Metal Remediation: From a Village to
	Keynote lecture	Environment, Director of	the Oil Patch
		ESRI, Swansea University,	
		United Kingdom	
10:20-10:55	Dr. Kiriaki	Foundation for Research	Structure and Dynamics of Bio-based
	Chrissopoulou	and Technology-Hellas,	Polyesters in the Bulk and Under
	Invited speaker	Institute of Electronic	Continement
		Structure and Laser,	
10.55 11.15	Coffee breek	Herakilon Crete, Greece	
Session II	Collee bleak		
Chair of the se	ssion Prof Ivo Leito		
11.15-11.45	Galina Garnaga-Budre	Director of Environmental	The Chemical Status of the Baltic Sea in
11.15 11.45	Invited speaker	Research Department	Lithuania: Current Status and Trends
		Lithuania	
11:45-12:15	Saulius Janulevicius	Limited liability company	Some Peculiarities of in-situ Soil and
	Invited speaker	"Grota", Lithuania	Groundwater Remediation in Lithuania
12:15-12:35	Prof. Dr. Henrikas	Vilnius University,	Leaching of Cu, Pb, Sn from e-waste and
	Cesiulis	Lithuania	Electrowinning in the Eco-friendly Solutions
	Oral presentation		
12:35-14:00	Lunch		
Session III,			
Chair of the se	ssion Prof. Arturs Viksna		
14:00-14:35	Prof. Dr. Przemyslaw	Department of Analytical	The Studies of Speciation in Environmental
	Niedzielski	Chemistry, Faculty of	Samples Using Hyphenated Techniques
	Invited speaker	Chemistry, Adam	with Atomic Spectrometry Detection
		Nicklewicz University,	
14.25 15.00	Dr. Agnoso Osito	Poznan, Polanu	Analysis of Particulate Matter Originated
14.55-15.00	Oral presentation	Latvia	During Burning of Scented Candles
15.00-15.20		Estonian Environmental	Analysis and Validation of Perfluorinated
13.00 13.20	Oral presentation	Research Centre Estonia	Compounds in Water, Sediment and Fish
			with LC-ESI-MS/MS
15:20-15:40	Coffee break	1	
15:40-17:30	Excursion to Vilnius University Library (Optional).		
15:40-17:30	Excursion to Vilnius University Life Sciences Center (Optional).		

### Date: Friday 26<sup>th</sup> October, 2018 Venue: Ministry of Environment of the Republic of Lithuania, Jakšto 4/9, Vilnius, 506 hall

8:00-9:00	Registration		
Session IV,			
Chair of the se	ssion Prof. Andrew R. Bar	ron	
9:00-9:35	Prof. Habil. Dr. Ewa	Faculty of Chemistry,	Very Precise Determination of Stable
	Bulska	University of Warsaw,	Isotopes of Ca, Mg and Sr by MC-ICPMS for
	Invited speaker	Poland	Environmental Purposes
9:35-10:10	Dr. Aleksey Etin	Limited liability company	A Story of an Eco-revolution in a Niche
	Invited speaker	"Veika", Lithuania	Industry
10:10-10:45	Dr. Maarja Opik	Department of Botany,	Why Should We Care of Soil Microbiota -
	Invited speaker	Institute of Ecology and	the Case of Arbuscular Mycorrhizal Fungi
		Earth Sciences, University	
		of Tartu, Estonia	
10:45-11:20	Coffee break		
Session V,			
Chair of the se	ssion Prof. Przemyslaw N	iedzielski	
11:20-11:50	Erika Mamaitiene	Environmental Protection	Determination of Pharmaceutical
	Invited speaker	Agency, Lithuania	Substances and Neonikotinoid Insecticides
			(EU-wide List of Substances to be
			Monitored in Accordance with Article 8b of
			Directive 2008/105 / EC) by Liquid
			Chromatography-Mass Spectrometry
11:50-12:15	Prof. Dr. Ivo Leito	University of Tartu,	Analytical Chemistry Education Activities at
	Oral presentation	Institute of Chemistry,	University of Tartu
		Tartu, Estonia	
12:15-12:35	Dr. Inna Melnyk	Institute of Geotechnics	Surface and Porosity Engineering of
	Oral presentation	of SAS, Kosice, Slovak	Aminosilica Nanoparticles for Different
		Republic and Chuiko	Applications
		Institute of Surface	
		Chemistry of NAS of	
		Ukraine, Kyiv, Ukraine	
12:30-14:00	Lunch		
Session VI,			
Chair of the se	ssion Dr. Maarja Opik		
14:00-14:30	Dr. Anatoli Popov	Institute of Solid State	Physics of Photostimulable Storage
	Invited speaker	Physics, University of	Phosphors – Progress Overview of Image
		Latvia, Riga, Latvia	Plate Development and Their Application in
			Physics, Biology and Life Sciences
14:30-14:50	Dr. Vilius Poskus	Vilnius University,	Trans Fatty Acids Separation by Silver
	Oral presentation	Lithuania	Nanoparticles Modified Monolitic Silica
			Column
14:50-15:10	Dr. Ingars Reinholds	Institute of Food Safety,	Mycotoxin Contamination in Herbal Teas
	Oral presentation	Animal Health and	from Latvia, Safety Assessment of Their
		Environment "BIOR",	Beverages
		Riga, Latvia	_

15:10-15:30	<b>Dr. Tadas Matijosius</b> Oral presentation	Center for Physical Sciences and Technology, Vilnius, Lithuania	Tribological Destruction of Anodized Al Waste of Different Alloys in Environment
15:30-15:50	Coffee break		
16:00-18:00	Poster presentations		
	Chair of the session Dr. Lina Mikoliunaite		
19:00-22:00	Conference dinner		

During the Gala Dinner the men's choir Avanti Vilnius will give concert. Young, charming and ambitious male vocal ensemble "Avanti Vilnius" (leader Ausra Liutkute) sing songs from Lithuanian and foreign authors



#### Date: Saturday 27<sup>th</sup> October, 2018

#### Venue: Ministry of Environment of the Republic of Lithuania, Jakšto 4/9, Vilnius, 506 hall

8:00-9:00	Registration		
Session VII,			
Chair of the se	ssion Dr. Kiriaki Chrissopo	pulou	
9:00-9:35	Dr. Vijayalakshmi	School of Engineering,	Application Carbon Nanomaterials and
	Velusami	Manchester Metropolitan	Carbohydrate Polymer Composites for
	Invited speaker	University, United	Sensing Environmental Toxins
		Kingdom	
9:35-10:10	Assoc. Prof. Dr. Ausra	Institute of Chemistry,	Electrochemical Oxidation -
	Valiuniene	Vilnius University,	Environmentally Friendly Way to Utilize
	Invited speaker	Lithuania	Cyanide Solutions
10:10-10:45	Dr. Natalia Tsyntsaru	Institute of Applied	Electrodeposited Catalysts Based on W-
	Invited speaker	Physics,	Rich Alloys for Sustainable Hydrogen
		Chisinau, Moldova	Production
10:45-11:00 Award of the best posters. Closing of the conference			

POSTER SESSION		
Friday 26 <sup>th</sup> October		
16:00	- 18:00	
<u>P 01</u>	A. Abola, Z. Gavare, E. Bogans,	DETERMINATION OF TOTAL MERCURY CONCENTRATION IN
	M. Strazds	EGGSHELLS OF BLACK STORKS
<u>P 02</u>	L. Alinauskas, Z. Stankeviciute,	SYNTHESIS AND CHARACTERIZATION OF POTASSIUM-DOPED
	A. Zarkov, G. Balciunas,	BIOACTIVE GLASS
	A. Kareiva, E. Garskaite	
<u>P 03</u>	B. Al-Saqarat, A. E. Al-	A NOVEL KAOLINITE-NPK MIXTURE AS AN
	Rawajfeh, B. Udvardi, M. R. Al-	ENVIRONMENTALLY FRIENDLY SLOW-RELEASE FERTILIZER
	Rbaihat, E. AlShamaileh	
<u>P 04</u>	V. Osipovaite, I. Ancutiene	COMPOSITIONAL AND MORPHOLOGICAL
		CHARACTERIZATION OF COPPER SELENIDES FILMS ON GLASS
<u>P 05</u>	S. Zukauskas, D. Palinauskas, A.	THE CARBAZOLE AND TRIPHENYLAMINE MOIETIES-BASED
	Ramanavicius, <b>G. Bagdziunas</b>	SEMICONDUCTORS FOR GLUCOSE BIOSENSORS
<u>P 06</u>	I. Barauskiene, E. Valatka	ELECTROCATALYTIC AND PSEUDOCAPACITIVE PROPERTIES OF
		LAYERED NICKEL-COBALT OXIDE COATINGS ON STAINLESS
		STEEL
<u>P 07</u>	Z. Dankova, <b>A. Bekenyiova,</b>	EXPERIMENTAL STUDY OF AS(V) ADSORPTION ONTO
	Z. Bujnakova, Z. Mitroova,	DIFFERENT ADSORBENTS
	D. Gesperova, I. Styriakova,	
	D. Styriakova and J. Briancin	
<u>P 08</u>	B. Brasiunas, A. Popov,	SYNTHESIS OF GOLD NANOPARTICLES USING REDUCING
	A. Ramanaviciene	SUGARS
<u>P 09</u>	<b>L. Busa,</b> L. Kepa, A. Viksna,	USE OF LA-ICP-MS AND IRMS DATA TO DISTINGUISH
	E. Bulska	BETWEEN ORGANICALLY AND CONVENTIONALLY GROWN
<b>D</b> 40		
<u>P 10</u>	A. Ciuladiene, A. Luckute,	INVESTIGATION OF RED BALLPOINT PEN INKS
D 44	A. Kareiva	
<u>P 11</u>	O. Demcnyna, B.Racniy,	
	V Babrivchuk B Bomanyuk	
	R. Musiv	
P 12	V.V.Sliesarenko., <b>O.A.Dudarko</b> .	FIXING OF Nd(III) IONS ON THE SURFACE OF MONO- AND
<u> </u>	I.V. Melnyk	BIFUNCTIONAL SILICA SBA-15 TYPE TO PROVIDE THEM
		LUMINESCENT PROPERTIES
P 13	I. Gabriunaite, A. Valiuniene	PHOSPHOLIPID BILAYER FORMATION ON FLUORINE DOPED
	,	TIN OXIDE
<u>P 14</u>	J. Gaidukevic, R. Trusovas,	LASER-INDUCED REDUCTION OF GRAPHENE OXIDE-DYE
	G. Niaura, I. Malisauskaite,	NANOCOMPOSITES: THE EFFECT OF DYE MOLECULES ON
	J. Barkauskas	GRAPHENE SHEETS QUALITY AND STRUCTURAL PROPERTIES
<u>P 15</u>	L. Glumbokaite, E. Dauksaite,	DEVELOPMENT OF A NOVEL AMPEROMETRIC GLUCOSE
	A. Kausaite-Minkstimiene	BIOSENSOR BASED ON GLUCOSE OXIDASE FUNCTIONALIZED
		POLY(PYRROLE-2-CARBOXYLIC ACID) PARTICLES

<u>P 16</u>	D. Godina, K. Meile,	STABILITY OF BIOMASS-BASED LEVOGLUCOSENONE IN
	A. Zhurinsh, R. Pomilovskis	AQUEOUS SOLUTIONS
<u>P 17</u>	R. Golubevas, A. Zarkov,	PREAPARATION OF POROUS GLASS-CERAMIC (GC) AND
	L. Alinauskas, A. Kareiva,	POLYMERIZED 1,6-HEXANDIOLDIACRYLATE (HDDA)
	E. Garskaite	COMPOSITE USING FREE RADICAL COPOLYMER
		CROSSLINKING
<u>P 18</u>	V. Grebnevs, A. Viksna,	DEVELOPMENT OF TXRF METHOD FOR DETERMINATION OF
	O. Purmalis, K.A. Gross,	CALCIUM AND PHOSPHORUS RATIO IN HYDROXYAPATITES
	L. Pluduma	
<u>P 19</u>	<b>D. Grendaite,</b> E. Stonevicius,	CHLOROPHYLL-A CONCENTRATION RETRIEVAL FROM
	J. Karosiene, K. Savadova, J.	SENTINEL-2 DATA IN LAKES IN LITHUANIA
<b>D D D</b>	Kasperoviciene	
<u>P 20</u>	<b>G. Inkrataite</b> , J. Aglinskaite, P.	PREPARATION AND ANALYSES OF CERIUM DOPED YTTRIUM
	Vitta, R. Skaudzius	ALUMINIUM GARNET, BORON NITRIDE AND POLYMER
D 24	D. hannaushan A. Kunsinta	
<u>P 21</u>	<b>K. Ivanauskas</b> , A. KUNCIUTE	
D 22	V Illevisione D Ivenevalue	
<u>P 22</u>	V. Oleviciene, <b>R. Ivanauskas</b> ,	
22.0	L. Salialuokas	
P 23	A Jansans A Osito	
<u>P 24</u>	<b>A. Jansons</b> , A. Osite.	
<u>P 25</u>	V. Jonauske, Th. C. K. Yang,	THE FORMATION OF CALCIUM HYDROXYAPATITE THIN FILMS
<b>D A C</b>	A. Kareiva	ON STAINLESS STEEL SUBSTRATE
<u>P 26</u>	<b>D. Karioniene,</b> D. Pupienis, S.	ASSESSMENT OF HEAVY METALS CONTENT IN BEACH
	Tautkus, A. Zarkov	SEDIMENTS ALONG THE SOUTHEASTERN BALTIC SEA COAST
D 27	M Akcomit Konorsko I C	
<u>P 27</u>	Torrosa, E. Bulska	INDACT DECTEONIC EXAMINATION OF WOOL'S KEDATIN
	TOTTESA, L. DUISKA	
P 28	<b>B Kozka</b> I A Drobniewska	APPLICATION OF PLEUROTUS OSTREATUS IN DEGRADATION
1 20	M Klimaszewska I Turlo	OF SELECTED ANTIDEPRESSANTS
	G. Nalecz-Jawecki.	
	Giebultowicz	
P 29	V. Saceviciene, N. Dukstiene,	STABILITY OF PES/PVC ARCHITECTURAL TEXTILE UNDER
	V. Krylova, S. Zalenkiene	ENVIROMENTAL EXPLOTATION
<u>P 30</u>	D. Kucharski, P. Drzewicz,	DETERMINATION OF TRIBUTYLTIN IN SEDIMENTS
	K. Mianowicz, A. Skowronek,	OF SZCZECIN LAGOON
	G. Nalecz-Jawecki,	
	J Giebultowicz	
P 31	A. Ruchajus, G. Dabrilaite-	CO2 SORPTION BY HETEROGENEOUS SORBENTS BASED ON
	Kudzmiene, A. Jaskunas, S.	ACTIVATED CARBON

<u>P 32</u>	K. D. Labsvards, L. Busa,	DETECTION OF C4 PLANT SUGAR IN ADULTERED HONEY
D 22	A Lourikanas E Valain	
<u>P 35</u>	A. Laurikenas, F. falcin	$M_{0}$ ( $H_{1}$ O) (ESSA), DME AND $M_{0}$ ( $H_{1}$ O) (ANSA), DME
D 24	M La consta 7 Deles de la	
<u>P 34</u>	V. Lazarenko, Z. Balcerbule,	THE VARIATION OF PHOSPHORUS, SULFUR AND NITROGEN
	V. Rudovica	IN LICHENS DEPENDING ON LOCALIZATION AREA
<u>P 35</u>	K. Meile, D. Godina,	CHALLENGES OF DETERMINING LEVOGLUCOSENONE BY
	A. Zhurinsh, R. Pomilovskis	UHPLC IN PYROLYSIS PRODUCTS
<u>P 36</u>	A. Minderyte, S. Butkute,	SOL – GEL SYNTHESIS OF ELECTROCHEMICALLY ACTIVE
	M. Skruodiene,	MOLYBDENUM OXIDE COATINGS
	M. Petruleviciene, I. Savickaja,	
	B. Sebeka, A. Selskis,	
	J. Juodkazyte, R. Ramanauskas	
<u>P 37</u>	M. Misevicius, V. Balevicius	ON THE CALCIUM SUBSTITUTION EFFECTS IN $Sr_{(4-x)}Ca_{(x)}AI_{14}O_{25}$
		DOPED WITH CERIUM
<u>P 38</u>	A. Moskina, A.I. Popov,	LUMINESCENCE CHARACTERIZATION OF AIN NANOTUBE/CsI
	V. Savchyn,	SCINTILLATOR AND AIN NANOTUBE/POLYMER COMPOSITES
	C. Balasubramanian,	FOR MEDICAL APPLICATION
	O.I. Aksimentyeva, E. Elsts,	
	L. Myasnikova, A. Barmina,	
	N. Zhanturina, S. Sagimbaeva,	
	D. Sergeyev, K.Shunkeyev	
<u>P 39</u>	A. Pakalniskis, L. Fadlyani, I.	ON THE SYNTHESIS AND CHARACTERIZATION OF BISMUTH
	Grigoraviciute-Puroniene, A.	FERRITE – BARIUM TITANATE SOLID SOLUTIONS
	Morkan, Z. Stankeviciute,	
	A. Zarkov, I. Morkan, R.	
	Skaudzius, A. Kareiva	
<u>P 40</u>	A. Pakalniskis, R. Skaudzius	INVESTIGATION ON AFFECT OF HYDROTERMAL SYNTHESIS
		CONDITIONS FOR EUROPIUM DOPED GADOLINIUM
		PHOSPHATE NANOPARTICLES SIZE AND MORPHOLOGY
<u>P 41</u>	R. Navikaite, R. Paleckiene	PREPARATION OF HUMIC SUBSTANCES AND THEIR
		APPLICATION FOR THE PRODUCTION OF FERTILIZERS
<u>P 42</u>	K. Paulauskaite,	CHANGING PROPERTIES OF UPCONVERTING NaGdF <sub>4</sub>
	I. Mikalauskaite,	NANOPARTICLES
	A. Beganskiene	
<u>P 43</u>	A. I. Rekertaite, P. Virbickas,	FORMATION AND CHARACTERISATION OF MIXED METALS
	A. Valiuniene	HEXACYANOFERRATES BASED AMPEROMETRIC GLUCOSE
		BIOSENSORS
<u>P 44</u>	J. Reklaitis, A. Nicolenco,	MAGNETIC PROPERTIES OF ELECTRODEPOSITED FE FILMS AS
	K. Mazeika, R. Davidonis,	POTENTIAL CATALYST WITH INCREASED EFFICIENCY
	K. Varsockaja, N. Tsyntsaru,	
	H. Cesiulis	

<u>P 45</u>	<b>D. Riekstina,</b> T. Krasta, A. Lescinskis	QUALITY CONTROL OF TRITIUM MEASUREMENTS IN ENVIRONMENTAL SAMPLES
<u>P 46</u>	T. Sabirovas, A. Valiuniene	ELETROCHEMICAL ANALYSIS OF ALUMINIUM SURFACE FOR HYBRID BILAYER FORMATION
<u>P 47</u>	I. Sendzikaite, V. Makareviciene	BIOTECHNOLOGICAL SYNTHESIS OF BIODIESEL FUEL BY INTERESTERIFICATION OF RAPSEED OIL WITH METHYL FORMATE
<u>P 48</u>	G. Burba, <b>D. Sinkeviciute,</b> N. Dukstiene	REMOVAL OF Pb <sup>2+</sup> , Ni <sup>2+</sup> , Zn <sup>2+</sup> AND CrO4 <sup>2-</sup> FROM ELECTROPLATING WASTEWATER BY ELECTROCOAGULATION
<u>P 49</u>	L. Sinusaite, I. Grigoraviciute- Puroniene, A. Antuzevics, A. Kareiva, A. Zarkov	EFFECT OF MANGANESE DOPING ON THE LOW- TEMPERATURE SYNTHESIS OF TRICALCIUM PHOSPHATE POLYMORPHS
<u>P 50</u>	A. Elmontaile, <b>K. Simksiene</b>	ALGAE
<u>P 51</u>	<b>E. Sprugis,</b> G. Vaivars, J. Kleperis	DEVELOPMENT OF POLYMER MEMBRANES FOR CATALYTIC CO <sub>2</sub> ABSORBTION
<u>P 52</u>	<b>Z. Stankeviciute,</b> J. Januskevicius, A. Kareiva	SOL-GEL SYNTHESIS OF NEODYMIUM SUBSTITUTED CALCIUM HYDROXYAPATITE
<u>P 53</u>	<b>R. Stokiene,</b> R. Ivanauskas, N. Petrsauskiene	STUDY THE SURFACE OF COBALT SULFIDE LAYERS ON POLYAMIDE
<u>P 54</u>	I. Styriakova, D. Styriakova	BACTERIAL TOLERANCE TO TOXIC ELEMENTS AND METALS ADSORPTION/METALLOID EXTRACTION N SOIL AND SEDIMENT HETEROTROPHIC LEACHING SYSTEMS
<u>P 55</u>	H. Lees, K. Siilak, P. Joul, P. Saar-Reismaa, <b>M. Vaher</b>	NONAQUEOUS CAPILLARY ELECTROPHORESIS METHOD FOR THE DETERMINATION OF PERFLUORINATED COMPOUNDS
<u>P 56</u>	<b>L. Valeikiene,</b> R. Paitian, I. Grigoraviciute-Puroniene, A. Kareiva	SOL-GEL SYNTHESIS OF Mg(X)/AI (X = Ca, Sr, Ba, Ni, Cu, Zn) LAYERED DOUBLE HYDROXIDES
<u>P 57</u>	<b>V. Valkovska,</b> A. Osite, G. Niaura, A. Kareiva	TEMPERATURE INFLUENCE OF HYDROTHERMAL PROCESSING ON PEROXIDE CONTENT AND CRYSTALLINITY OF CALCIUM AND PARTIALLY SUBSTITUTED STRONTIUM HYDROXY- PEROXYAPATITES
<u>P 58</u>	<ul> <li>E. Zubryte, A. Gefeniene,</li> <li>D. Kauspediene, S. Jankauskas,</li> <li>R. Ragauskas</li> </ul>	TREATMENT OF ANODIZED ALUMINIUM DYEING WASTEWATER BY DRINKING WATER DEIRONING RESIDUALS

# Keynote and Invited Speakers



## FLEXIBLE APPROACHES TO WATER TREATMENT AND METAL REMEDIATION: FROM A VILLAGE TO THE OIL PATCH

Andrew R. Barron<sup>1,2,3\*</sup>

<sup>1</sup>Energy safety Research Institute, Swansea University, Bay Campus, Swansea, SA1 8EN, UK
 <sup>2</sup>Department of Chemistry, Rice University, 6100 Main Street, Houston, Texas 77005, USA
 <sup>3</sup>Department of Materials Science and Nanoengineering, Rice University, 6100 Main Street, Houston, Texas 77005, USA

\* e-mail: <u>a.r.barron@swansea.ac.uk;</u> <u>arb@rice.edu</u>

The lack of simple, effective, remediation technologies is a significant hindrance to the quality of living in developing regions of the world. As such water represents the largest global resource issue. Purification (reuse) of industrial waste water is an increasing problem, especially in heavy industry, e.g., produced water for oil industry. At the local level there is a need for low cost/low energy purification of water in energy poverty regions, and a further need for water for agriculture in arid regions. A simple flexible solution that allows for industrial waste water control as well as water treatment at the local "village" is desirable. The technology must be low cost, easily deployable, easily regenerated and recycled, and have low operation costs. Two compatible technologies based upon controlled surface functionalization will be discussed involving ceramic surfaces and carbon nanotubes. We show the chemical functionalisation of alumina ceramic microfiltration membranes (0.22 µm pore size) with cysteic acid creates a superhydrophilic surface, allowing for separation of hydrocarbons from oil well produced waters without fouling. The rejection coefficients was >90%. The separation of hydrocarbons from water when the former have hydrodynamic diameters smaller than the pore size of the membrane is due to the zwitter ionically charged superhydrophilic pore surface. Membrane fouling is essentially eliminated, while a specific flux is obtained at a lower pressure (<2 bar) than that required achieving the same flux for the untreated membrane (4–8 bar). In contrast, the preparation and characterization of a supported-epoxidized carbon nanotube (SENT) via the growth of multi walled carbon nanotubes (MWNTs) onto a quartz substrate. Subsequent epoxidation provides sufficient functionality to enable adsorbent of heavy metals ( $Cd^{2+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$ ,  $Hg^{2+}$ ,  $Ni^{2+}$ , and  $Pb^{2+}$ ) from aqueous solution with initial concentrations (60–6000 ppm) chosen to simulate high industrial wastewater contamination. The SENT adsorption efficiency is >99.4% for all metals and the saturation concentration is significantly greater than observed for either GO or acid treated MWNTs. Details of field trials of both technologies will be presented



Images of field demonstrations of superhydrophilic membrane applications in (a) Guatemala City and (b) Utah, USA **References** 

- 1. S. J. Maguire-Boyle, J. E. Huszman, T. J. Ainscough D. Oatley-Radcliffe, A. A. Alabdulkarem, S. F. Al-Mojil, and Andrew R. Barron, *Sci. Reports*, **7** (2017) 12267.
- 2. P. N. Alagappan, J. Heimann, L. Morrow, E. Andreoli, and A. R. Barron, Sci. Reports, 7 (2017) 6682.

## STRUCTURE AND DYNAMICS OF BIO-BASED POLYESTERS IN THE BULK AND UNDER CONFINEMENT

#### K. Chrissopoulou

#### Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, 70013, Heraklion Crete, Greece

#### kiki@iesl.forth.gr

Biobased and biodegradable polymers have received much attention over the last three decades and a number of industries tend to substitute petroleum-based with bio-based intermediate materials in order to reduce the environmental footprint of their products [1-3]. Among such materials, bio-based aliphatic polyesters have attracted considerable attention due to the combination of biodegradability, biocompatibility and their physical and/or chemical properties, which are, in many cases, comparable to the respective properties of more common and widely utilized polymers. The biodegradability of such polymers can be influenced by many factors like their macromolecular characteristics, their morphology as well as their thermal, surface and mechanical properties. On the other hand, the investigation of the structure and dynamics of polymer chains in the bulk and, more recently, under confinement, has attracted the scientific interest both because it greatly affects many of the macroscopic properties and because of the complexity it exhibits over many length- and time-scales [4]. At the same time, the behavior of polymers in the bulk appears to be very different from that close to surfaces due to the different interactions. This behavior can be studied especially in intercalated polymer / layered silicate nanohybrids (PLSN) which offer a unique avenue to study the behavior of macromolecules under nanoscopic confinement [5,6].

The present work investigates the structure and the dynamics of two bio-based polyester polyols in the bulk and close to surfaces when the polymers are intercalated within the galleries of a hydrophilic sodium montmorillonite, Na<sup>+</sup>-MMT [7]. The morphology of the neat polymers as well as the structure of the nanohybrids are investigated with X-ray diffraction and their thermal properties are studied by differential scanning calorimetry. One of the investigated polyesters is amorphous whereas the second one is a semi-crystalline polymer with an intriguing thermal behavior. Hybrids have been synthesized in a broad range of compositions and intercalated structures are always obtained. Dielectric relaxation spectroscopy was utilized to study the polymer dynamics. It revealed multiple relaxation processes for the neat polymers both below and above their glass transition temperatures whereas, in the nanocomposites, similarities and differences are observed depending on the specific mode of dynamic process. The results are compared with the ones of hyperbranched polymers of similar chemistry but non-linear architecture [8].

Acknowledgements. Supported by the project "National Research Infrastructure on nanotechnology, advanced materials and micro/nanoelectronics" (MIS 5002772) and by COST Action MP1202-HINT.

- 1. A. L. Holmberg, K. H. Reno, R. P. Wool, T. H. Epps, Soft Matter, 10 (2014) 7405-7424.
- 2. H. Nakajima, P. Dijkstra, K. Loos, Polymers 9 (2017) 523 (1-26).
- 3. A. Merlettini, M. Gigli, M. Ramella, C. Gualandi, M. Soccio, F. Boccafoschi, A. Munar, N. Lotti, M. L. Focarete, Biomacromolecules **18** (2017) 2499-2508.
- 4. M. D. Ediger, Annu. Rev. Phys. Chem., **51** (2000) 99-128.
- 5. K. Chrissopoulou, K. S. Andrikopoulos, S. Fotiadou, S. Bollas, C. Karageorgaki, D. Christofilos, G. A. Voyiatzis, S. H. Anastasiadis, Macromolecules 44 (2011) 9710-9722.
- 6. K. Chrissopoulou, S. H. Anastasiadis, Soft Matter 11 (2015) 3746-3766.
- 7. K. Androulaki, K. Chrissopoulou, D. Prevosto, M. Labardi, S. H. Anastasiadis, Biomacromolecules submitted (2015).
- K. Androulaki, K. Chrissopoulou, D. Prevosto, M. Labardi, S. H. Anastasiadis, ACS Appl. Mater. Inter., 7 (2015) 12387-12398.

## THE CHEMICAL STATUS OF THE BALTIC SEA IN LITHUANIA: CURRENT STATUS AND TRENDS

#### G. Garnaga-Budrė<sup>1\*</sup>

<sup>1</sup>Environmental Protection Agency, Environmental Research Department, A Juozapavičiaus g. 9, LT-09311 Vilnius, Lithuania \*Corresponding author, e-mail: galina.garnaga@aaa.am.lt

The chemical status of the Baltic Sea in Lithuania is evaluated according to the concentrations of the 45 priority substances and certain other pollutants from EQS Directive 2013/39/EU and other substances of national concern. All pollutants are included in Lithuanian National Environment Monitoring Programme which is updated every 6 years. New monitoring programme for 2018-2023 has been prepared according to the requirements of EU Water Framework Directive, Marine Strategy Framework Directive, Stockholm Convention (POPs) and national strategy. Environmental Protection Agency is a main institution responsible for the monitoring of pollutants in Lithuania. Monitoring is performed in water, sediments and biota (fish and mussels). Pollutants are monitored at up to 19 stations in the Baltic Sea and Curonian Lagoon. Sampling stations are located in different water types of coastal and transitional waters and also in the open sea. Chemical status (good or not good) is determined for each water type by the comparing the concentrations of the substances with Environmental Quality Standards or threshold values.

Helsinki Commission (HELCOM) in 2018 has prepared the Second Holistic Assessment of the state of the Baltic Sea. Concentrations of some hazardous substances were used as core indicators of the state of the Baltic Sea. The assessment has shown that such substances as polybrominated diphenyl ethers, perfluorooctane sulphonate, polyaromatic hydrocarbons, tributyltin, mercury, cadmium and lead are of specific concern for the whole Baltic Sea, including Lithuania, – these substances are often fail the threshold values [1].

#### References

1. HELCOM, State of the Baltic Sea – Second HELCOM holistic assessment 2011-2016. Baltic Sea Environment Proceedings 155, 2018.

#### SOME PECULARITIES OF IN-SITU SOIL AND GROUNDWATER REMEDIATION IN LITHUANIA

#### S. Janulevičius\*, A. Marcinonis, R. Tekoriene

UAB "GROTA", Eišiskių plentas 26, LT-02184 Vilnius, Lithuania \*S. Janulevičius, e-mail: <u>saulius@grota.lt</u>

The beginning of soil and groundwater remediation practice in-situ as well as ex-situ in Lithuania should be dated to 1989 when the remediation of shallow groundwater aquifer at the former Vilnius oil base territory was started [1].

The main contaminants were/are oil products, that dominate at the approximately 65% of all contaminated sites. Pesticides (26%) and heavy metals (9%) prevail at the other 35% of the sites. 69% of all contaminated sites were or targeted to be remediated using ex-situ methodology, i.e. commonly excavating the contaminated soil, spreading it on the special fields and processed with bio- or other preparations. But often to reach deep contamination with ex-situ methods could be complicated. So 31% of the contaminated sites could be desired to treat or/and treated already in-situ, i.e., at the places of the soil/groundwater natural being.

In total about 30 sites were or being remediated in-situ during all the period till 2018 [1]. Overall majority of the sites were remediated using "pump and treat" method. This is a common method for cleaning up contaminated groundwater. Groundwater with contaminants is pumped from wells to an above-ground treatment system that removes the contaminants. Pump and treat systems also are used to "contain" the contaminant plume and to keep it from reaching water wells, streams, and other natural resources [2]. However, using this method in the cases with oil contaminated soil, only 50-80% of contamination could be removed [3]. The free phase oil product (LNAPL) largely could be removed, but not the residual phase that remains sorbed in the soil.

With the regimentation of the environmental requirements the need of advanced in-situ remediation methods became extremely relevant. So the first dual phase and soil vapor extraction equipment was purchased from USA in 1998 and started the operation in Lithuania. Using this method and applying the high vacuum pump oil contamination could be removed from the soil up to 90-95% [3].

Applying the above mentioned methods for in-situ soil/groundwater remediation though often does not allow reaching the nowadays allowable limits of the soil contamination. This is relevant when the remediation time is limited to 2-3 years. Therefore some microbiological investigations were carried out at the Šiauliai former military airport with the aim to isolate the aboriginal oil oxidizing bacteria. In a case of successful results the bacterial preparation will be multiplied and used for the further in-situ remediation after the usage of the above mentioned physical methods. On the basis of Šiauliai airport case study the comparison of the main in-situ soil/groundwater remediation methods are overlooked in the presentation.

#### References

1. D. Januševičiūtė, A. Marcinonis, S. Janulevičius ir kt. Cheminėmis medžiagomis užteršto grunto ir požeminio vandens valymo metodai. LGT prie AM, UAB "GROTA", Vilnius, 2015, p. 40, 105-107

- 2. A Citizen's Guide to Pump and Treat. EPA 542-F12-17, September, 2012.
- 3. V. Juodkazis, A.Marcinonis. Aplinkos hidrogeologija. Vilniaus universitetas, 2008, p. 429, 433.

#### LEACHING OF Cu, Pb, Sn FROM E- WASTE AND ELECTROWINNING IN THE ECO-FRIENDLY SOLUTIONS

A. Dulksnis<sup>1,2</sup>, <u>H. Cesiulis<sup>1,2\*</sup></u>, N. Tsyntsaru<sup>1,3</sup>

<sup>1</sup>Vilnius University, Faculty of Chemistry and Geosciences, Naugarduko 24, Vilnius, Lithuania; <sup>2</sup>JSC Elektronikos Perdirbimo Technologijos, Medeinos 45, Vilnius, Lithuania; <sup>3</sup>Institute of Applied Physics, Academiei 5, Chishinau, Moldova \*E-mail: henrikas.cesiulis@chf.vu.lt

The European Commission's Waste Electrical and Electronic Equipment (WEEE) Directive requires that member states recycle and recover all electrical waste and electronic equipment rather than simply disposing it in landfill sites. E-waste is composed of a large number of components such as Cu, Al, Fe, Sn, Pb, Zn, Ag, Au, Pd, etc. The components are removed through separate treatment and recycling processes. It is convenient to separate Cu, Pb and Sn at first stages of WEEE treatment, because their compounds hydrolyzed and form colloidal hydroxides that block filters of e-waste equipment. Thus, the aim was to investigate leaching and recovery of Cu, Pb and Sn by electrowinning using environmentally friendly solutions.

*Experimental procedure*: Working electrodes for leaching tests were: Cu rod, Pb (99,998%), Sn (99,998%) wires (Alfa Aesar) with exposed areas of 1 cm<sup>2</sup>; the reference and counter electrodes were Ag/AgCl<sub>sat</sub> and graphite respectively. The electrochemical experiments were performed at room temperature in a cell connected to the Potentiostat/ Galvanostat AUTOLAB N302. The corrosion current density of Cu, Pb and Sn was evaluated using the potentiodynamic polarization technique in 3-electrode cell. Cu plate (as cathode, surface area 8 cm<sup>2</sup>) and graphite (anode) were used as a working electrode for electrowinning in 2-electrode system.

*Results*: Actually, the leaching of metals and formation of soluble compounds is a process of enforced corrosion. Influence of pH, H<sub>2</sub>O<sub>2</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>, C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> on Cu, Pb and Sn leaching was investigated. Corrosion of Cu, Pb and Sn in glycine solution is extremely slow due to the acid adsorption on the metal surface. Adsorbed layer of glycine inhibits further metal dissolution especially in the case of Sn. Corrosion rate for Cu, Pb and Sn is highest in citric acid with the addition of ammonium persulfate at pH:  $1.8 \div 3$ ,  $5 \div 7$  and  $3.8 \div 5.8$  respectively. In the strongly acidic solutions (pH < 5), corrosion rate of lead and tin drops down and corrosion rate of copper decreases when solutions become less acidic (pH > 3) (Fig. 1). Influence of pH and applied voltage on weight of electrodeposited metals using flat and metal foam electrodes was investigated. The electrowinning was performed using 2-electrodes cell and the compact film containing Pb, Sn and Cu could be obtained on the cathode at bath voltage:  $\Delta E = 3.5 \text{ V}$  (pH 5.7) or  $\Delta E = 3 \text{ V}$  (pH 7.5).





Acknowledgments: This research has received funding from Horizon 2020 research and innovation programme under MSCA-RISE-2017 grant agreement No. 778357.

#### THE STUDIES OF SPECIATION IN ENVIRONMENTAL SAMPLES USING HYPHENATED TECHNIQUES WITH ATOMIC SPECTROMETRY DETECTION

#### P. Niedzielski

Adam Mickiewicz University in Poznań, Faculty of Chemistry, Department of Analytical Chemistry,898 Umultowska Street, 61-614 Poznań, Poland e-mail:pnied@amu.edu.pl

Hyphenated techniques are a new and constantly developing tools of speciation analysis, allowing direct determination of the forms of the elements. These techniques in one analytical system group two (or more) independent techniques - usually separation techniques and selective detection techniques. Separation of the forms takes place in a chromatographic system - gas chromatography or high-performance liquid chromatography (or capillary electrophoresis), while for the detection are used the spectrometric techniques: absorption (AAS) or atomic emission spectrometry (OES), atomic fluorescence (AFS), inductively coupled (ICP) or microwave induced (MIP) plasma with emission detection (OES) or mass spectrometry (MS). A special place among spectrometric techniques used in hyphenated techniques is occupied by absorption or emission atomic spectrometry. Although the use of these techniques as chromatographic detectors has a long history, it has not been yet possible to commercialize the instruments (as in the case of HPLC-ICP-MS) and analytical instruments are still being set up from scratch in laboratories.

Several examples of instruments of atomic absorption or emission spectrometry as a detection techniques in liquid chromatography will be presented. The exemplary applications of speciation analysis in the study of markers of processes taking place in the environment will be indicated.

#### ANALYSIS OF PARTICULATE MATTER ORIGINATED DURING BURNING OF SCENTED CANDLES

I. Blūma<sup>1</sup>, <u>A. Osīte<sup>1,\*</sup></u> S. Osipovs<sup>2</sup>,

<sup>1</sup> Faculty of Chemistry, University of Latvia, Jelgavas Street 1, Riga, LV-1004, Latvia 2 Faculty of Natural Sciences and Matematics, University of Daugavpils, Parādes Street 1, Daugavpils LV-5401, Latvia

\*Corresponding author, e-mail: agnese.osite@lu.lv

Indoor air pollution – mainly increased concentrations of small size particulate matter (<PM<sub>1</sub>) originated from combustion process, e.g. cooking, smoking, candle and incense burning still is the topic often discussed in the scientific papers showing the strong evidence that exposure to particles pollution is associated not only with significant impact on the health effects in general but also with respiratory system inflammation, oxidative stress and elevated levels of oxidatively damaged DNA in cultured cells of animals and humans [1]. Some reports assume that fumes from scented candles made of petroleum derivative, may be more toxic than candles made of the natural ingredients like stearin and beeswax [2]. Scented candles' burning indoors can release various volatile organic compounds (VOC), aldehydes, hydrocarbons, alcohols and number of carcinogens such as naphthalene, anthracene and pyrene. Scented candles additives, e.g. fragrance and aroma oil, are responsible for high VOCs emissions [3]. There are more different additives used in candles to improve the burning performance and aesthetic appearance. For example in certain types of candles, metals such as, zinc, tin and lead are added to the wick to meliorate mechanical stability as well as colouring pigments may content heavy metals [4].

During the current research a close test chamber with clean air supply was formed for combustion experiments (Fig.1). Sampling and analysis of particulate matter was realized by Grimm Aerosol Spectrometer EDM 365 and Ambient NO<sub>x</sub> Monitor APNA-370 (Fig.2). Different types of scented candles (containing soya, stearin, paraffin, rape, palm oil wax) were used. Particles emitted during burning were counted and also collected onto sorbents such us aminopropyl silica gel and activated carbon. VOCs determination was done by GC-MS, realizing sample pre-treatment with solvent desorption and for trace metal analysis by ICP-MS aerosol acidic extraction from quartz filters were used.



Fig. 1. Schematic figure of experimental set-up



**Fig.** 2. PM<sub>x</sub> and NO<sub>x</sub> mass concentrations during burning *Tromborg* scented candle

#### References

[1] Skovmand, A., Gouveia, A.C.D., Koponen, I.K., Moller, P., Loft, S., Roursgaard, M. Lung inflammation and genotoxicity in mice lungs after pulmonary exposure to candle light combustion particles. *Toxicology Letters*, **2017**, 276, 31-38.

[2] Orecchio, S. Polycyclic aromatic hydrocarbons (PAHs) in indoor emission from decorative candles. *Atmospheric Environment*, **2011**, 45, 1888-1895.

[3] Ahn, J.H., Kim, K.H., Kim, Y.H., Kim, B.W. Characterization of hazardous and odorous volatiles emitted from scented candles before lighting un when lit. *Journal of Hazardous Materials*, **2015**, 286, 242-251.

[4] Pagels, J., Wierzbicka, A., Nilsson, E.Isaxon, C., Dahl, A., Gudmundsson, A., Swietlicki, E, Bohgard, M. Chemical composition and mass emission factors of candle smoke particles. *Aerosol science*, **2009**, 40, 193-208.

#### ANALYSIS AND VALIDATION OF PERFLUORINATED COMPOUNDS IN WATER, SEDIMENT AND FISH WITH LC-ESI-MS/MS

<u>S. Saaver<sup>1,2</sup></u>, R. Rebane<sup>1,2\*</sup>

<sup>1</sup>Estonian Environmental Research Centre, Marja 4d, 10167 Tallinn, Estonia <sup>2</sup>University of Tartu, Ravila 14a, 50411 Tartu, Estonia \*Corresponding author, e-mail: riin.rebane@klab.ee

The analysis of perfluorinated compounds (PFCs) in environmental matrices is challenging, as the concentrations are generally low, but the risk of contamination is high. Sample preparation is a critical step and it is necessary to minimize the possibility of contamination. In this study a modified ion pair extraction (IPE) method to quantify PFCs in sediment and fish samples successfully applied and validated [1].

A large volume injection (LVI) method was validated and used to quantify PFCs in different water matrices. Isotope internal standard of every analyte was applied to correct matrix effects. The recoveries of the analytes were 92% - 106% for water matrix, 93% - 119% for fish matrix and 86% - 103% for soil matrix whereas the achieved limit of quantitation (LoQ) values were 1.3 - 14.9 ng/L for water, 0.19 - 0.28 µg/kg for fish and 0.14-0.41 for soil samples.

During method development, many issues were encountered in relation to analysis. For example that different standard solutions for PFOS were different and in addition to linear PFOS isomer some also contained branched version (Figure 1). Linear PFOS concentration in Dr. Ehrenstorfer was 59% of the expected concentration, whereas the sum of the isomer peaks made up 104% of the expected total PFOS concentration. For Fluka, the linear peak was 91% of the expected PFOS concentration and total PFOS concentrations reached 126%. Consequently, isi s recommended to use a mixture of PFOS



Figure 1. Chromatograms of PFOS solutions.

isomers as this mimics more realistically real-life situations.

It was also observed that there are multiple sources for PFC contamination and following recommendations are given for method development in a routine laboratories: purchase another set of chemicals (check for PFCs before use); where possible use dosators for liquid chemicals; use HPLC grade water, check all vessels and syringe filters for PFCs; apply as little sample preparation as possible; for water analysis prefer LVI; use PFC trapping column for eluents [2]; use isotopically labelled internal standards for every PFC; use vessels made of PE for sample collection and PP tubes for the extraction procedure; confirm for standard PFOS solutions if the nominal concentration corresponds to the linear PFOS or to the total amount of isomers; total PFOS concentrations should be measured instead of linear PFOS; a reagent blank can be used to correct the sample results.

31 surface water, 8 stormwater and 41 sediment samples collected all over Estonia were analysed and four (out of 8 analysed) PFCs were found in quantitative amount. The most frequently detected analyte heptafluorobutyric acid (PFBA) was found in 26% of the water samples with a maximum concentration of 137 ng/L.

#### References

1. S. Kaupmees, R. Rebane, Intern. J. Environ. Anal. Chem., 97 (2017) 697-709.

2. P. K. W. Stone, L. Cote, J. Gushue, R. J. Letcher and S. Chu, Agilent App. Note, 5990-5313 (2010).

#### VERY PRECISE DETERMINATION OF STABLE ISOTOPES OF CA, MG AND SR BY MC-ICPMS FOR ENVIRONMENTAL PURPOSES

#### E. Bulska, L. Halicz, J. Karasiński, A. Krata, and M. Wojciechowski

a) Faulty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland b) Geological Survey of Israel, 30 Malkhei Israel, st.,Jerusalem 95501, Israel

The measurements of calcium, magnesium and strontium stable isotopic ratios, due to their variability in nature, play an important role in biology, medicine and geology, because they provide the information about fractionation in plants, animals and related with them changes in biological cycles. The applicability of Ion Chromatography (IC) coupled to Multicollector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) for on-line separation of calcium, magnesium and strontium from a matrix followed by the determination of isotope ratios of 44Ca/42Ca, 26Mg/24Mg and 87Sr/86Sr was explored. Various instrumental setups were employed to enable continuous separation of both analytes from the sample matrix by IC followed by MC-ICPMS. The performance of two separation columns IonPac CS16 (ID 5mm or ID 3mm) connected with appropriate CERS500 suppressors (4mm or 2mm) using dry and wet plasma conditions was compared. With the use of ID 3mm column and 2 mm suppressor it was possible to apply dry plasma mode with Aridus II desolvation system. Mass discrimination and instrument drift were corrected by using the natural constant 86Sr/88Sr ratio as an internal standard or by using sample – standard bracketing method for 44Ca/42Ca and 26Mg/24Mg isotope ratio of SRM 915 a and DSM-3 as standard, respectively. Good accuracy and high precision of isotope ratios (generally of 0.15% expressed as 2SD) were achieved for wet and dry plasma modes. The sensitivity of MC-ICP MS measurements with dry plasma was 25 times higher in comparison to wet plasma conditions. Robustness and applicability of the method was demonstrated for matrix-rich natural water and rock samples.

#### **Acknowledgments**

This research was financial supported by the National Centre of Science (NCN, Poland), project UMO-2014/13/B/ST4/04503, in the years 2015 - 2018.

- Karasinski J., Bulska E., Halicz L., Wojciechowski M., Krata A.A., "Direct determination of δ44/42Ca isotope ratio by ion chromatography/low-resolution multicollector ICPMS", J Mass Spectrom., 53 (2018) 78-82;
- 2. Karasinski J., Bulska E., Wojciechowski M., Halicz L., Krata A.A., "High precision direct analysis of magnesium isotope ratio by ion chromatography/multicollector-ICPMS using wet and dry plasma conditions", Talanta, 165 (2017) 64-68;
- Karasinski J., Bulska E., Wojciechowski M., Krata A.A., Halicz L., "On-line separation of strontium from a matrix and determination of the 87Sr/86Sr ratio by Ion Chromatography/Multicollector-ICPMS", J. Anal. At. Spectrom., 31 (2016) 1459-1463;

#### AN ECO-REVOLUTION IN A NICHE INDUSTRY

#### Dr. Aleksey Etin<sup>1,\*</sup>

<sup>1,\*</sup> Veika UAB, Baltosios Vokes 37, LT02243, Vilnius, Lithuania. letin@veika.lt

The niche where our company has strong background is wallpaper industry. It is a global industry with multibillion Euro annual sales [1]. Currently, the vast majority of the wallpaper industry is based on plasticized polyvinyl chloride (PVC) materials that pose environmental challenge. Approximately 6 years ago, we started Ecodeco project, which goal is to change the materials that are used in the wallpaper industry worldwide. The cleaner polyolefin based alternative - Ecodeco offers significant advantages over plasticized PVC in the environmental aspect [2].

The main difference between the two alternatives is the presence of liquid plasticizers (mostly infamous phthalate) in the plasticized PVC, while the softness of Polyolefin based Ecodeco is controlled by a comonomer content. In contrast to a monomer, plasticizers (up to 40% of total PVC mass) are not chemically bound to the polymer and are migrating out of the compound during its life cycle. Approximately 30% of initial plasticizer content evaporates during production phase and the rest is slowly migrating to the environment in the shops, homes and, finally, landfills. The wallpaper industry has gone tremendous steps in order to continue working with PVC – starting from a complicated production equipment to trap and incinerate the emitted gases to creating standards of emission testing of wallpaper. However, it is clear that it is impossible to trap all the emissions and, therefore, the smell nearby factories as well as in rolls themselves is clearly distinguishable. Ecodeco material has no emission during production and its emission in house is by several orders of magnitude below the plasticized PVC emission.

The author will give a detailed review of a project that is driven by our company for over 6 years and has passed through stages of basic lab development to pilot production and actual commercial implementation. Actual reaction of markets is mixed. The leaders of the industry are mostly concerned with the fact that the new eco-material may ruin their business model and do not support the Ecodeco project. In our opinion, this is one of the key points why eco-material change in any industry may be restricted. On the other hand, there is still no legislation that actually would help to promote eco-materials by restricting wallpaper production based on plasticized PVC. The support comes from the smaller players and the only actual way to be successful is to produce eco-material with the same price to quality ratio as compared to the standard material.

- 1. The global wallcoverings association annual report (2017)
- 2. A.Etin, EP2915839A1 (2014)

#### WHY SHOULD WE CARE OF SOIL MICROBIOTA – THE CASE OF URBUSCULAR MYCORRHIZAL FUNGI

#### <u>M. Öpik</u>

University of Tartu, 40 Lai Street, 51005 Tartu, Estonia

Soil biodiversity, its micro- and macrobiota, is increasingly recognized as provider of important functions of nature to the humans. These ecosystem services range from air and water regulation to aboveground biodiversity and landscape diversity support to sustainable agriculture and food security.

Arbuscular mycorrhizal (AM) fungi can be considered as keystone members of soil microbiota via their functions to plant nutrition, environmental and biotic stress mitigation and soil health maintenance. Therefore, there is increasing focus on the application of AM fungi in agriculture, restoration and conservation, including both direct inoculation with fungi as well as fostering growth and functioning of existing, indigenous species.

I will summarise current knowledge on the biodiversity of AM fungi from local to global scales. I will focus on how anthropogenic activities influence diversity and functioning of AM fungi and present recent understanding on how current agricultural practices relate to AM fungal performance, and how this in turn relates to crop yield. Further, I'll provide an overview of how AM fungi contribute and can be used to restoration of important nature value habitats, as well as restoration of vegetation in abandoned mines.

Finally, I'll conclude with ways to develop monitoring approaches of AM fungal performance in agricultural and natural soils, to be better able to apply locally appropriate management practices that support soil microbiota.

#### DETERMINATION OF PHARMACEUTICAL SUBSTANCES AND NEONIKOTINOID INSECTICIDES (EU-WIDE LIST OF SUBSTANCES TO BE MONITORED IN ACCORDANCE WITH ARTICLE 8B OF DIRECTIVE 2008/105 / EC) BY LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY

#### E. Mamaitienė

The Environmental Protection Agency, Juozapavičiaus st. 9, LT-09311 Vilnius, Lithuania

The EU-wide list of substances to be monitored in accordance with Article 8b of Directive 2008/105 / EC includes chemical substances that may pose a significant risk to or via the aquatic environment, but insufficient monitoring data is available [1]. This report present analytical methods developted for detection of hormones (17- $\alpha$ -ethinylestradiol, 17- $\beta$ -estradiol, estrone), macrolide antibiotics (erythromycin, azithromycin, clarithromycin) and neonicotinoid insecticides (imidacloprid, thiacloprid, thiamethoxam, clothianidin, acetamiprid) by ultra high pressure liquid chromatography with Time of fligth Mass spectrometry (UHPLC-TOF MS) technic.

The preparation of water samples before analyses is based on solid phase extraction (SPE), using HLB cartridges. Method presented in this work allow to detect these analites with maximum acceptable method detection limit (ng/L) and even with smaller concentrations.

#### References

1. <u>https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32018D0840</u>

#### ANALYTICAL CHEMISTRY EDUCATION ACTIVITIES AT UNIVERSITY OF TARTU

#### I. Leito<sup>1,\*</sup>

<sup>1</sup>University of Tartu, Institute of Chemistry, Ravila 14a, 50411 Tartu, ESTONIA \*Corresponding author, e-mail: <u>ivo.leito@ut.ee</u>

The presentation gives an overview about the current analytical chemistry education activities at University of Tartu.

The first part of the presentation addresses the master's programmes **Excellence in Analytical Chemistry** *Erasmus Mundus* (EACH, <u>www.analyticalchemistry.eu</u>) and **Applied Measurement Science** (AMS, <u>ams.ut.ee</u>). These are 120 ECTS international master's programmes. AMS is a hybrid programme covering, physical measurements, chemical analysis, testing and quality assurance while EACH is focused on analytical chemistry. Both programmes have strong coverage of metrology in chemistry topics [1] as well as notable environmental analysis component and directly rely on the related research in our group [2,3].

The second part presents experience of running two MOOCs (Massive Open Online Courses) "Estimation of measurement uncertainty in chemical analysis" (sisu.ut.ee/measurement/uncertainty) [4] and "LC/MS Method Validation" (sisu.ut.ee/lcms\_method\_validation/). The latter course is largely based on the recently published two-part tutorial review on validation of LC-MS methods [5,6]. Teaching in the "MOOC mode" is compared to conventional university teaching as well as to short training courses for professionals. In chemistry MOOCs are no real competitors for the conventional university degree programmes. Instead they can be seen as useful add-ons: the on-line course material can be used by students of conventional courses as a reference point for explanations and definitions, source of sample calculation files, for self-testing. The self-testing possibility using the on-line tests of the MOOC has proved especially useful in our experience.

#### References

[1] I. Leito, Accreditation Qual. Assur. 20 (2015) 229–231.

[2] A. Teearu, S. Vahur, T. Rodima, K. Herodes, W. Bonrath, T. Netscher, S. Tshepelevitsh, A. Trummal, M. Lõkov, I. Leito, J. Mass Spectrom. 52 (2017) 603–617.

[3] I. Helm, G. Karina, L. Jalukse, T. Pagano, I. Leito, Environ. Monit. Assess. 190 (2018) 313.

[4] I. Leito, I. Helm, L. Jalukse, Anal. Bioanal. Chem. 407 (2015) 1277–1281.

[5] A. Kruve, R. Rebane, K. Kipper, M.-L. Oldekop, H. Evard, K. Herodes, P. Ravio, I. Leito, Anal. Chim. Acta 870 (2015) 8–28.

[6] A. Kruve, R. Rebane, K. Kipper, M.-L. Oldekop, H. Evard, K. Herodes, P. Ravio, I. Leito, Anal. Chim. Acta 870 (2015) 29– 44.

#### SURFACE AND POROSITY ENGINEERING OF AMINOSILICA NANOPARTICLES FOR DIFFERENT APPLICATIONS

<u>I.V. Melnyk</u><sup>1,2\*</sup>, V.V. Tomina<sup>2</sup>, N.V. Stolyarchuk<sup>2</sup>, A.P. Lebed<sup>3</sup>, I.M. Furtat<sup>3</sup>, M. Kanuchova<sup>4</sup>, D. Behunova<sup>1</sup>, M. Vaclavikova<sup>1</sup>

<sup>1</sup>Institute of Geotechnics of SAS, Watsonova 45, 04001 Kosice, Slovak Republic
<sup>2</sup>Chuiko Institute of Surface Chemistry of NAS of Ukraine, Generala Naumova 17, 03164 Kyiv, Ukraine
<sup>3</sup>National University of Kyiv-Mohyla Academy, Skovoroda 2, 04070 Kyiv, Ukraine
<sup>4</sup>Technical University of Kosice, Letna 9, 04200 Kosice, Slovak Republic
\*Corresponding author, e-mail:in.melnyk@gmail.com

Aminosilica nanospheres could be used as simple and useful carriers for different applications in nanomedicine, catalysis, adsorption, or tribology (Fig.). However they require definite characteristics, such as size, porosity, content and distribution of amino groups on the particle's surface.

Therefore, this research is devoted to one-step sol-gel synthesis of aminosilica nanoparticles. We investigated the effect of components ratio, synthesis temperature, structuring agent variations (tetraethoxysilane to bissilanes), additional methyl or phenyl groups' introduction on the particle size, functional groups concentration, porosity, zeta potential, adsorption of acid red and methylene blue dyes [1-4]. We also studied  $Cu^{2+}$  uptake and antimicrobial properties of some aminosilica particles with/without adsorbed copper(II) ions. Summarizing, such materials can have 150-460 nm size, 1.8-4.1 mmol/g of aminopropyl groups, surface area from 40 to 800 m<sup>2</sup>/g, and sorption capacities to acid red from 81 to 262 mg/g and methylene blue from 55 to 146 mg/g. Cu(II) ions adsorption was 1.2-2.6 mmol/g, forming complexes 2/1 and 1/1. Some aminosilica nanoparticles with Cu<sup>2+</sup> demonstrated up to 97.8% of antibacterial activity against *S. aureus* during 60 min [4].

The suggested approaches provide control over the properties of the final materials necessary to create smart nanomaterials.

The research is financed from the SASPRO project No. 1298/03/01.

- 1. I.V. Melnyk, Chemistry Journal of Moldova, 9(1) (2014) 123-127.
- 2. N.V.Stolyarchuk, M.Barczak, I.V.Melnyk, Yu.Zub, In Nanophysics, Nanophotonics, Surface Studies, and Applications, Springer, 2016, V.183, p.415-425
- V.Tomina, I.Melnyk, Y.Zub, A.Kareiva, M.Vaclavikova, G.Seisenbaeva, V.Kessler, Beilstein Journal of Nanotechnology, 8 (2017) 334–347
- S.S. Kotsyuda, V.V. Tomina, Y.L. Zub, I.M. Furtat, A.P. Lebed, M. Vaclavikova, I.V. Melnyk, Applied Surface Science, 420 (2017) 782–791



Fig. Some possibilities for application of the silica spheres with amino groups

#### PHYSICS OF PHOTOSTIMULABLE STORAGE PHOSPHORS – PROGRESS OVERVIEW OF IMAGE PLATE DEVELOPMENT AND THEIR APPLICATION IN PHYSICS, BIOLOGY AND LIFE SCIENCES

#### A. I. Popov

<sup>1</sup>Institute of Solid State Physics University of Latvia, 8 Kengaraga, LV-1063 Riga, Latvia <u>e-mail:popov@latnet.lv</u>

A great deal of research has been performed during the last three decades on photostimulabled storage phosphors. Such luminescent materials have found a lot of attractive applications in many different fields of radiation imaging. In general, a storage phosphor functions as follows: ionizing radiation generates metastable electron and hole trap centers, whose concentration is proportional to the incident dose. The centres with trapped electrons are photostimulable, so upon optical excitation by laser photon each electron recombines with appropriate hole center to produce photostimulated luminescence (PSL), which is proportional to the density of the locally trapped electron and hole pairs and thus proportional to the locally absorbed dose of incident ionizing radiation [1-5].

When a photostimulated storage phosphor (e.g. BaFBr:Eu) is mixed with a neutron converter (e.g.  $Gd_2O_3$  or <sup>6</sup>LiF), it becomes sensitive to thermal neutrons [6,7]. Neutron-sensitive image plates (NIPs) mage of such storage phosphors have great potential as two-dimensional integrating thermal neutron detectors. Scanning the NIP with a focused laser and a photomultiplier faced by an optical filter allows simultaneous excitation and detection of luminescence from the colour centres so that stored information is read out spot-by-spot. The wide dynamic range, the high spatial resolution and the use of large active areas make these systems also interesting for application as thermal neutron detectors in neutron diffraction and neutron radiography experiments.

The thermal neutron-sensitive image plates (NIP's), used on the LADI-III Laue diffractometers at ILL (Grenoble, France), COALA at ANSTO (Australia) and etc., offer several advantages as cold- and thermalneutron detectors, notably excellent resolution, wide dynamic range, and easy incorporation in large-solid angle detectors. In this presentation we will also summarize the current status of research in the field of neutron storage phosphors with emphasis on the specific requirements for both luminescence storage phosphor and neutron converter. Short overview of the image plate application for radiation imaging and dosimetry in physics, chemistry, biology and life sciences will be finally presented.

- 1. K. Takahashi, K. Kohda, J. Miyahara, Y. Kanemitsu, K. Amitani, S. Shionoya, J. Lumin., 31&32 (1984) 266-268.
- 2. A. Kalnins, I. Plavina, A.I. Popov, A. Tale, J. Phys.: Condens. Matter, 3 (1991) 1265.
- 3. L.E. Trinkler, M.F. Trinkler, A.I. Popov, Phys. Status Solidi (b), 180 (1993) K31-K34.
- 4. P.F. Braslavets, A. Kalniņš, I. Pļaviņa, A.I. Popov, B.I. Rapoport, A. Tāle, Phys. Status Solidi (b), 170 (1992) 395-401.
- 5. A.I. Popov, I.Plavina, Nucl. Instrum Meth B, **101** (1995) 252-254
- 6. A.V. Sidorenko, A.J.J. Bos, P. Dorenbos, C.W.E. van Eijk, P.A. Rodnyi, I.V. Berezovskaya, V.P. Dotsenko, A.I. Popov, J. Appl. Phys., 95 (2004) 7898-7902.
- 7. A.I. Popov, J.Zimmermann, G.J. McIntyre, C. Wilkinson, Optical Materials 59 (2016) 83-86.

#### TRANS FATTY ACIDS SEPARATION BY SILVER NANOPARTICLES MODIFIED MONOLITIC SILICA COLUMN

#### V. Poškus\*, V. Vičkačkaitė

Department of Analytical and Environmental Chemistry, Vilnius University, Naugarduko St. 24, LT-03225 Vilnius, Lithuania poskus.vilius@gmail.com

Fatty acids contained in fat samples are most commonly measured by gas chromatography after their extraction and conversion into methyl esters. However, even with the use of long and efficient capillary columns cis/trans isomers of fatty acids are hardly separated and their peaks often overlap. To separate cis/trans isomers, a pre-separation by silver-ion solid phase extraction (Ag<sup>+</sup> -SPE) can be employed [1]. Ag<sup>+</sup>-SPE is based on the ability of silver ions to form weak reversible charge transfer complexes with  $\pi$  electrons of the double bonds of unsaturated fatty acids [2-3]. Monolithic silica columns have greater (through-pore size)/(skeleton size) ratios than conventional particle-packed columns, resulting in higher permeability in comparison with particulate columns [4]. The potential of silver ion chromatography in combination with monolithic HPLC columns for the separation and concentration of  $\omega$ 3 long-chain polyunsaturated fatty acids esters has been demonstrated [5]. Nevertheless in its ionic state, silver is not stable for a long period of time, especially under the exposure of light. Because of the delocalization of charge, silver nanoparticles (Ag NPs) tend to have affinity toward electron-rich unsaturated bonds [6]. Therefore, for the separation of cis/trans fatty acids instead of ionic silver, Ag NPs could be used.

We have successfully synthesized monolithic silica SPE column by employing a one-pot acid–base two-step reaction catalyzed by acetic acid and hydrolysis product of urea. The modification of the monolith with aminopropyl groups was achieved by the reaction of (3-aminopropyl)triethoxysilane and silanol groups on the monolith surface. A successful modification of the monolith with aminopropyl groups was proved by thermogravimetric analysis that demonstrated a resolved exothermic peak between 300 and 350 °C due to the pyrolysis of aminopropyl groups on the silica surface. Aminopropyl groups modified monolith was further washed with silver nitrate solution. Due to a lower reduction potential of the formed amine complex of silver in comparison to silver ions, formaldehyde could be used as a reducting agent. Uncomplexed Ag<sup>+</sup> ions cannot be reducted by formaldehyde, so their excess was washed out after the reaction. The distribution and morphology of Ag NPs embedded in the monolith was observed by TEM and the presence of metallic silver was confirmed by EDX. Prepared SPE columns were tested for fractionation of rape seed oil fatty acids methyl esters (FAMEs) spiked with elaidic acid methyl ester. The Ag NPs-embedded monolithic sorbent showed good stability and separation of fatty acids based on a number and configuration of double bounds. The presented method allows eliminating about 90% of cis isomers of FAMEs from the trans fraction.

- 1. V. Poškus, V. Vičkačkaitė, G. Brimas, Chemija, 27(3), (2016), p.179.
- 2. S. Momchilova, B. Nikolova-Damyanova, J. Sep. Sci., 26,(2003), p. 261
- 3. M. Dolowy, a. Pyka, J. Chem. 2015, ID 120830 (2015)
- 4. T. Ikegami, N. Takana, Annu. Rev. Anal. Chem.9, (2016), p.317.
- 5. P. Fagan, C. Wijesundera, J. Sep. Sci., 36, (2013), p.1743.
- 6. Z. D. Pozun, K. Tran, A. Shi, R. H. Smith, G. Henkelman, J. Phys. Chem., 115, (2011), p.1811

## MYCOTOXIN CONTAMINATION IN HERBAL TEAS FROM LATVIA, SAFETY ASESSMENT OF THEIR BEVERAGES

#### I. Reinholds<sup>1,\*</sup>, E. Bogdanova<sup>1,2</sup>, I. Pugajeva<sup>1</sup>, V. Bartkevics<sup>1,2</sup>

<sup>1</sup>Institute of Food Safety, Animal Health and Environment "BIOR", Lejupes Street 3, LV-1076 Riga, Latvia <sup>2</sup>Faculty of Chemistry, University of Latvia, Jelgavas Street 1, LV-1004, Riga, Latvia \*Corresponding author, e-mail: Ingars.Reinholds@bior.lv

Herbal teas have been frequently applied in medicine and also used as daily beverages. Environmental and biologic factors may influence the contamination status of such products with mold producing mycotoxins during the pre-harvest periods, post-harvest procession and storage [1-2]. Aflatoxin B<sub>1</sub> (AFB<sub>1</sub>) and the total four aflatoxins are the only one mycotoxins with regulated permissible levels of 2 ng/g for AFB<sub>1</sub> in medical herbs according to recommendations set by the European Pharmacopeia, whereas ochratoxin A has been regulated in certain condiments at 15-20 ng/g [3]. Those carcinogenic human toxins have been frequently reported in coffee, tea and herbs [4]. *Fusarium* mycotoxins belong to a wide range of contaminants, which may present hazards to human health. Compounds such as zearalenone (ZEN), deoxynivalenol (DON), a trichothecenes, fumonisins, enniatins etc. may occur in teas and their infusions [5-6].

In the present study several herbal teas obtained from drug stores in Latvia were analysed for the presence of twelve mycotoxins by liquid chromatography – mass spectrometry methods. The study indicated 90% of the samples as contaminated with one to eight mycotoxins. *Fusarium* compound deoxynivalenol was the most frequently presented mycotoxin presented at high contamination levels (in 55% of the tested raw teas). ZEN and DON were determined in infusions of tested tea samples – the transfer rate for DON ranged between 32-100%. The population survey data on the consumption of herbal teas showed a comparatively similar tea intakes for different types of tea for residents of Latvia. Compared to> 300 mL of black or green tea consumption, the average daily intake of herbal teas was equal to one received cup (250-260 mL). In view of the availability of these data, a risk assessment was carried out assuming that one tea mug (1 to 2 g of tea) is taken on an average daily basis. Risk assessment data showed that tea infusions made from the tea samples analysed in this study were relatively safe for the consumers. A high incidence of multi-contamination of 56% determined in the case of tested dry tea samples raise concerns of future challenges for safety management of herbal teas.

Acknowledgement The funding of this research by ERDF funds for "Post-doctoral Research Aid" in Latvia (Project No. 1.1.1.2/VIAA/1/16/219) is acknowledged.

- 1. Kosalec, J. Cvek, S. Tomić, 60 (2009) 485-500.
- 2. N.K. Dubey, P.K. Mishra, A. Kedia, B. Prakash, In Microbial Diversity and Biotechnology in Food Security; Ed. R.N. Kharwar, R.Raghuwanshi, R.S. Upadhyay, Springer, New Delhi, 2014, p. 495-504.
- 3. L. Zhang, X.W. Dou, C. Zhang, A.F. Logrieco, M.H. Yang, Toxins, 10 (2018) 65-00.
- 4. F. Malir, V. Ostry, A. Pfohl-Leszkowicz, J. Toman, I. Bazin, T.Roubal, 6 (2014) 3438-3453.
- 5. L. Santos, S. Marín, V. Sanchis, A.J. Ramos 89 (2009) 1802-1807.
- 6. N. Pallarés G. Font, J. Mañes, E. Ferrer 65 (2017) 10282–10289.

#### TRIBOLOGICAL DESTRUCTION OF ANODIZED AI WASTE OF DIFFERENT ALLOYS IN ENVIRONMENT

#### T. Matijošius<sup>\*</sup>, I. Valsiūnas, S. Asadauskas

Center for Physical Sciences and Technology, Saulėtekio av. 3, LT-10257 Vilnius, Lithuania \*Corresponding author, e-mail: tadas.matijosius@ftmc.lt

About 60 million tons of aluminum (Al) are produced annually, a large portion of which is anodized by electrochemical oxidation process. Anodization is effective at improving surface hardness, paintability, wear and corrosion resistance. However, Al waste from beverage cans to transport or construction items can cause environmental problems if not disposed properly due to harboring insects, plugging natural streams, etc. It was estimated that it takes more than 100 years for an aluminum can to disintegrate due to corrosion [1, 2]. However, possible wear in nature settings has not been considered yet, although such waste is exposed to abrasion by dust, sand, moving soil layers, ice sheets, river beds, etc. In this study friction and wear was evaluated on anodized Al alloys in an attempt to simulate their potential decomposition regime under dry natural conditions.

Anodization of 1050, 3003, 5005, 6082 and 7075 Al alloys was performed in aqueous sulfuric/oxalic electrolyte as described previously [3] to obtain coatings with ~20  $\mu$ m in thickness. Ball-on-plate mode on the tribometer (Anton Paar TriTec SA) was selected for friction tests in linearly reciprocal configuration with 6 mm OD steel balls under 10 N load, 2 cm/s velocity and 8 mm cycle length. Wear measurements after 500 friction cycles were evaluated with profilometer Surtronic S25.



Fig. 1. Coefficient of Friction, COF (left) and wear profiles (right) of anodized Al alloys after 500 friction cycles under 10 N load

Testing showed that tribological behavior of anodized coatings depended on the alloy type very significantly, Fig. 1. Lowest wear track depth (2  $\mu$ m) was observed on 7075 alloys possibly due to high content of Cu (2.1 wt.%) and Zn (7.7 wt.%) inter metallic compounds, responsible for surface hardness. 3003 alloys had highest wear track depth (5  $\mu$ m) suggesting their faster destruction under tribological exposure in the environment. Counterintuitively, 3003 showed low initial COF, which might represent reduced surface hardness and increased surface deformation under 10 N load.

Wear rates of anodized coatings might be important for the environment and dramatically different performance of anodized Al alloys should be considered when assessing the effects on ecosystems by Al accumulation.

- 1. S.A. Buza, K.A. Buza, K. Pllana, J. Trends. Dev. Mach. Assoc. Technol., 18 (2014) 179-182.
- 2. J. Rossiter, J. Winfield, I. Ieropoulos, Proc. SPIE, 9798 (2016) 1-10.
- 3. T. Matijošius, A. Ručinskienė, S. Asadauskas, Proc. 18th Conf. Jun. Res., 11 (2015) 71-78.

#### APPLICATION OF CARBON NANOMATERIALS AND CARBOHYDRATE POLYMER COMPOSITES FOR SENSING ENVIRONMENTAL TOXINS

V. Velusamy<sup>1</sup>\*, S. Palanisamy<sup>2</sup>, T. C.K. Yang<sup>3</sup>

<sup>1</sup>Division of Electrical and Electronic Engineering, School of Engineering, Manchester Metropolitan University, Chester Street, Manchester M1 5GD, United Kingdom <sup>2</sup>Department of Chemical Engineering, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao East Road, Taipei-106, Taiwan \*Corresponding author, e-mail: V.Velusamy@mmu.ac.uk

The synthesis of composites of carbon nanomaterial/carbohydrate polymers has gained heightened attention as novel electrode materials for environmental toxins detection [1]. The combined unique physicochemical properties of carbon nanomaterial with carbohydrate polymers could leads to improved sensor characteristics to detect the environmental toxins [2]. The present talk includes the development of graphene-based cellulose microfiber (GR-CMF) composite sensor materials for detection of catechol (CC) and fenitrothion (FNTN). The laccase immobilized GR-CMF composite biosensor electrode was used for detection of CC, and the composite was prepared by simple sonication of GR in CMF solution [2]. The amperometric response of the biosensor was linear over the concertation of CC ranging from 0.2 to 209.7µM with the detection limit of 0.085µM. The fenitrothion sensor was fabricated using a CMF supported reduced graphene oxide (RGO) modified electrode, and was synthesized by a simple electrochemical reduction of graphene oxide-CMF composite [3]. Differential pulse voltammetric response of the fabricated composite electrode is linear for detection of FNTN in a range up to 1.134 mM with a detection limit of 8 nM. The fabricated CC biosensor is highly selective in the presence of potentially active biomolecules and phenolic compounds. The biosensor also accessed for the detection of CC in different water samples and shows good practicality with an appropriate repeatability.



- 1. M. Govindhan, B.R. Adhikari, A. Chen, RSC Adv., 4 (2014) 63741–63760.
- 2. S. Palanisamy, K. Thangavelu, S.M. Chen, V. Velusamy, M.H. Chang, T.W. Chen, F.M.A. Al-Hemaid, A. Ali, S.K. Ramaraj, Sensors and Actuators B: Chemical, 243 (2017) 888-894.
- S. Palanisamy, S.K. Ramaraj, S.M. Chen, T.C.K. Yang, P.Y. Fan, T.W. Chen, V. Velusamy, S. Selvam, Sci. Rep. 7 (2017) 41214.
- V. Velusamy, S. Palanisamy, S.W. Chen, S. Balu, T.C.K.Yang, C.E. Banks, Talanta https://doi.org/10.1016/j.talanta.2018.09.055.

#### ELECTROCHEMICAL OXIDATION – ENVIRONMENTALLY FRIENDLY WAY TO UTILIZE CYANIDE SOLUTIONS

#### <u>A. Valiūnienė<sup>1\*</sup></u>

<sup>1</sup>Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko st. 24, LT – 03225, Vilnius, Lithuania. \*Corresponding author, e-mail:ausra.valiuniene@chf.vu.lt

Cyanides are used as the main material in many industries such as textile, plastics, paints, photography, electroplating, agriculture, food, medicine and mining/metallurgy [1]. Some forms of cyanide are very strong and fast acting toxins. Despite being toxic, cyanides of low concentration can be found in various plants and microorganisms. However, most of the cyanides in the environment come from metal finishing and mining industries. In some wastewaters cyanide concentration can reach 100000 mg L<sup>-1</sup>. It is obvious that such effluence is ecologically dangerous, and so, in many countries it is an obligation to treat these wastewaters before spilling them into the environment. By the suggestion of many countries and environmental protection agencies, allowed  $CN^-$  concentration limits [2] are 0.01 - 0.5 mg L<sup>-1</sup>. 0.07 mg L<sup>-1</sup>  $CN^-$  is considered safe for both acute and long-term exposure in drinking water by the World Health Organization (WHO) guidelines while the European Union (EU) specifies 0.05 mg  $CN^-$  per litre. As the environmental regulations have become stricter about cyanide usage, the developing removal processes have become more needed.

The most adequate tool for treatment of aqueous effluent is the electrolytic process, ideally suited for these days, when environmental considerations are always the most important. Electrochemical oxidation can be used for destroying highly concentrated cyanide wastes (>50,000 mg L<sup>-1</sup> CN<sup>-</sup>). However, widely used studies to develop an electrolytic cyanide utilization process have not yet been developed. According to the scientific literature [3] the electrochemical oxidation is a very economical and environmentally friendly cyanide destruction process. The main efforts of investigators are concentrated on the selection of the anode material, which should ensure high electrochemical activity in parallel to chemical and physical stability as well as finding an economical and simple method for high-yield cyanide oxidation. Many of the proposed electrodes are too expensive or complicated in preparation. It was demonstrated [4] that platinized Ti electrodes may serve as anodes for effective electrochemical oxidation of cyanides and replace commonly used metal Pt electrodes.

However, in order to create a technological process, some additional experiments should be carried out, determining optimal electrode parameters as well as conditions for electrolysis and kinetic parameters of electrochemical reaction [5]. Taking kinetic parameters of electrochemical reaction into account, it is possible to maximize the efficiency of the process and to design economically effective method for degradation of cyanide wastewaters.

- 1. N. Kuyucak, A. Akcil, Miner Eng, **50-51** (2013) 13-29.
- 2. R.R. Dash, A. Gaur, C. Balomajumder, J Hazard Mater, 163 (2009) 1-11.
- 3. L. Hartinger, Handbook of Effluence Treatment and Recycling for the Metal Finishing, 2nd ed. Finishing Publications Ltd, Stevenage, 1994.
- 4. Valiūnienė, G. Baltrūnas, V. Keršulytė, Ž. Margarian, G. Valinčius, Process Saf Environ Prot, 91(4) (2013) 269-274.
- 5. Valiūnienė, Ž. Margarian, R. Valiūnas, React Kinet Mech Cat, 115 (2015) 449-461.

#### ELECTRODEPOSITED CATALYSTS BASED ON W-RICH ALLOYS FOR SUSTAINABLE HYDROGEN PRODUCTION

N. Tsyntsaru<sup>1,2,\*</sup>, E. Vernickaitė<sup>1</sup>, P. Globa<sup>2</sup>, H. Cesiulis<sup>1</sup>

<sup>1</sup>Vilnius University, Naugarduko str. 24, LT-03225, Vilnius, Lithuania <sup>2</sup>Institute of Applied Physics, Academiei str. 5, MD-2028, Chisinau, Moldova \*Corresponding author, e-mail: ashra\_nt@yahoo.com

Hydrogen evolution technology is considered as a key element for the sustainable economic growth and generation of clean future energy [1]. Mostly precious platinum is applied in electro-catalytic systems for hydrogen evolution reaction (HER), thus the development of new cost effective and durable materials which possess high catalytic activity for HER is necessary. Accordingly, in this study W-rich alloys with iron group metals, namely Co, Ni and Fe, are presented as alternative cathodes for sustainable hydrogen generation in alkaline environment.

Ni-W, Co-W and Fe-W alloys having up to 30 at.% of W in their composition were electrodeposited onto stainless steel substrate under galvanostatic mode from environmentally friendly citrate electrolyte. The electrocatalytic activity of the prepared alloys was studied by linear scan voltammetry in 30 wt.% NaOH medium in the temperature range from 25 to 65°C. Extrapolation of the polarization curves obtained at different temperatures, in the coordinates lni -  $\Delta E$  to value  $\Delta E=0$  makes it possible to determine the exchange current densities (ECD) that describe the ability of electrode to reduce hydrogen ions from the electrolyte.

It was found, that the higher content of W results in an enhanced HER catalytic activity and the electrodes with ~30 at.% of W demonstrates the highest ECD at 25°C. A significant improvement of catalytic activity for W-rich coatings with increasing of the temperature has been noticed. The electrocatalytic activity at 65°C is decreasing in the following order Co-31W>Ni-30W>Fe-32W (in at.%) (Table 1). In order to enhance the catalytic activity, the efforts to achieve the higher content of refractory metal in the alloys have been made. For such purpose highly concentrated acetate electrolyte has been investigated as alternative electrolyte to citrate containing solution. This bath allowed to deposit only 25 at.% of W, but up to ~50 at.% of Mo could be reached. Among all investigated electrodes the Mo-rich alloys demonstrated the highest catalytic activity towards hydrogen evolution reaction (Table 2).

Table 1. Exchange current densities for
W-rich electrodes at 65°C.

Sample	ECD, mA/cm <sup>2</sup>
Ni-30 at.% W	14.8
Co-33 at.% W	20.9
Fe-32 at.% W	0.82

**Table 2.** Exchange current densities for Mo-rich electrodes at 65°C.

Sample	ECD, mA/cm <sup>2</sup>
Ni-54 at.% Mo	25.4
Co-52 at.% Mo	46.2
Fe-54 at.% Mo	14.2

Acknowledgments: This research has received funding from Horizon 2020 research and innovation program under MSCA-RISE-2017 grant agreement No. 778357 and project No 09.3.3-LMT-K-712-08-0003.

#### Reference

1. A. Züttel, A. Borgschulte, L. Schlapbach, Hydrogen as a future energy carrier. Wiley-VCH Verlag GmbH&Co. KGaA, Weinheim, 2008.

# Poster session



#### DETERMINATION OF TOTAL MERCURY CONCENTRATION IN EGGSHELLS OF BLACK STORKS

#### A. Abola<sup>1,\*</sup>, Z. Gavare<sup>1</sup>, E. Bogans<sup>1</sup>, M. Strazds<sup>2</sup>

<sup>1</sup>Institute of Atomic Physics and Spectroscopy, University of Latvia, Skunu Str. 4, LV-1050, Riga, Latvia <sup>2</sup>Institute of Biology, University of Latvia, Miera Str. 3, LV-2169, Salaspils, Latvia \*Corresponding author, e-mail: anda.abola@lu.lv

As the population of black storks (*Ciconia nigra*) in Baltic countries is decreasing [1], ornithologists for years are trying to understand the reasons. The research carried out in 2014 [2] revealed unexpectedly high concentration of Hg in blood of juvenile Black storks.

To investigate the possible causes of mercury exposure in non-invasive form, bird related items such as feathers and eggshells can be used as it is well known, that the birds excrete considerable amounts of pollutants through feather moult (e.g. heavy metals), and females can excrete pollutants in contents of their eggs, as a result juvenile birds can receive limited amount of pollutants from their mother via egg yolk.

In this work we measured total mercury concentration in eggshells of black stork by means of thermal decomposition. Analysis were done with spectrometer RA-915M and its attachment pyrolyzer PYRO-915+ (Lumex, Russia). Samples were collected from various nesting places in Latvia.

The determined concentration of total mercury in analysed samples of eggshells varied from as few as 4 ng/g and reaching 50 ng/g. Our measurements also confirmed that various parts of egg have different mercury concentrations [3] – where possible we measured eggshells and inner eggshell membranes separately and results showed significant differences – 5 to 10 times higher concentrations for inner eggshell membranes than outer hard shells.

The results indicate that juvenile black storks receive some amount of mercury from their mother, however it is expected that major source of contamination could be their food items, so the continuation of this study will be the mercury concentration measurements in food samples.

- 1. E.A. Tamas, Biologia 66/5: 912-915, 2011
- J. Černova. Ekoloģiskā piesārņojuma kumulācija melnā stārķa (Ciconia nigra) organismā. Internatūras prakses atskaites darbs. Latvijas Lauksaimniecības Universitāte. Jelgava (2015).
- 3. S. H. Peterson et al., Environ. Toxicol. Chem. 2017; 36:2417–2427
## SYNTHESIS AND CHARACTERIZATION OF POTASSIUM-DOPED BIOACTIVE GLASS

#### <sup>1</sup>L. Alinauskas, <sup>1</sup>Z. Stankeviciute, <sup>1</sup>A. Žarkov, <sup>2</sup>G. Balciunas, <sup>1</sup>A. Kareiva, <sup>1</sup>E. Garskaite

<sup>1</sup>Institute of Chemistry, Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania

<sup>2</sup>Scientific Institute of Thermal Insulation, Vilnius Gediminas Technical University, Linkmenu st. 28, Vilnius LT-08217, Lithuania

Skeletal injuries are the major causes of morbidity and mortality. Bone loss might be due to various causes including congenital defects, traumatic accidents, and diseases such as osteoporosis, reduction of alveolar bone as a consequence of tooth extraction and chronic periodontal breakdown that causes loss of teeth and osteonecrosis [1].

All bioactive materials form an interfacial bond with adjacent tissue. However, the time dependence of bonding, the strength of the bond, the mechanism of bonding, and the thickness of the bonding zone differ for the various materials. Bioactive glasses, in fact, are characterized by a higher bioactivity index compared to HA, and specific compositions, such as the widely used 45S5 Bioglass<sup>®</sup>, are able to bond to soft tissues as well as to hard ones [2].

Thus, in order to discover the ideal biomaterial, several synthetic bone substitutes have been developed. The desired requirements for synthetic bone grafts include bonding ability to bone and/or soft tissues, osteoinduction, osteoconduction, enhanced angiogenesis and upregulation of specific genes that control the osteoblast cell cycle [3].

In recent years, the doping of bioactive glasses with Mg, Zn, Cu, Sr, Ag and some other elements have been found beneficial, greatly affecting the biological turnover and the process of bones formation. As the potassium is one of the important minor components of hard tissues, helps to reduce the chances of osteoporosis in elderly ages and is involved in apatite biomineralization, therefore its doping can be an important consideration in improving the biomedical properties [4].

Here we report the synthesis of potassium doped glass-ceramic by sol-gel method. The cylindrical-shaped specimens were prepared by mechanical pressing synthesized powders using hydraulic press. The formation of hydroxyapatite (HAp) layer on the glass surface upon immersion in simulated body fluid (SBF) was observed via FE-SEM, XRD and FT-IR spectroscopy.

Keywords: bioglass, ceramics, sol-gel, bone tissue.

#### References

1. S. Paulo et al., Bisphosphonate-related osteonecrosis of the jaw: specificities, Oncol. Rev. 8 (2014) 44-49.

2. L.L. Hench, Bioceramics: from concept to clinic, J. Am. Ceram. Soc. 74 1487-1510 (1991).

3. Manuel M. Ferreiraa et al., Can the regenerative potential of an alkali-free bioactive glass composition be enhanced when mixed with resorbable  $\beta$ -TCP?, Ceramics International 44 (2018) 5025–5031.

4. Muhhamad Shoaib et al., Potassium-doped mesoporous bioactive glass: synthesis, characterization and evaluation of biomedical properties Materials Science and Engineering: C 75, (2017), 836-844.

## A NOVEL KAOLINITE – NPK MIXTURE AS AN ENVIRONMENTALLY FRIENDLY SLOW– RELEASE FERTILIZER

B. Al-Saqarat<sup>1</sup>, A. Eid Al-Rawajfeh<sup>2</sup>, B. Udvardi<sup>3</sup>, M. R. Al-Rbaihat<sup>4</sup>, <u>E. Al-Shamaileh<sup>\*4</sup></u>

<sup>1</sup>University of Jordan, Department of Geology, Amman, Jordan <sup>2</sup>Tafila Technical University, Department of Chemical Engineering, Tafila, Jordan <sup>3</sup>Mining and Geological Survey of Hungary, Budapest, Hungary <sup>4</sup>University of Jordan, Department of Chemistry, Amman, Jordan <u>ehab@ju.edu.jo</u>; <u>ehabju@gmail.com</u>

In the present study, spectroscopic and structural characterization of a novel mixture of kaolinite-NPK to serve as an environmentally friendly slow-release fertilizer using FTIR, XRD and DSC, is described. methods are used. Kaolinite is an environmentally friendly substance that exhibits good structural properties when used as a carrier of chemical fertilizers. Mixtures of kaolinite and NPK fertilizer were prepared by mechanochemical ball milling with three different mass ratios (kaolinite : NPK = 1:3, 1:1 and 3:1). The milling parameters were varied in order to obtain the best mixture consistency and performance of a slow-release fertilizer. These include milling time (60, 120, and 180 min) and rotational speed (200, 400 and 700 rpm). The studied NPK fertilizers are urea (CON<sub>2</sub>H<sub>4</sub>), ammonium phosphate ((NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>), and potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>). The result indicated that a mass ratio of kaolinite : NPK of 3:1 and a milling duration of 120 min at a rotational speed of 600 rpm represent the most suitable conditions to synthesize a novel kaolinite-NPK slow-release fertilizer. Similar milling parameters were found for all the tested fertilizers proving the success of using kaolinite: NPK mixture as a slow-release fertilizer.

Key Words: NPK fertilizers, Kaolinite, Mechanochemical, Milling, FTIR, XRD, DSC, Slow-release fertilizers.

## COMPOSITIONAL AND MORPHOLOGICAL CHARACTERIZATION OF COPPER SELENIDES FILMS ON GLASS

#### V. Osipovaitė, I. Ancutienė\*

Department of Physical and Inorganic Chemistry, Kaunas University of Technology, Radvilenu str. 19, LT-50254 Kaunas, Lithuania \*Corresponding author, e-mail: ingrida.ancutiene@ktu.lt

The interest for copper selenides films is motivated by their applications in solar cell technology. Photoelectrochemical processes based on polycrystalline metal chalcogenide (MX, where M=Zn, Cd or Cu; X=S, Se or Te) electrodes are being considered, due to their ease of preparation, low thickness, economic demand for starting chemical amounts and low environmental impact [1,2]. With a band gap range 2.1–2.3 eV and high absorptivity, copper selenide films are promising candidates for photo-electrochemical purposes [3].

In this study copper selenides films were formed on glass slides of dimension 10 mm×10 mm. Slides were washed using liquid soap and water, then they were cleaned ultrasonically in acetone at 40 °C for 10 min, then rinsed with distilled water and dried. Selenide films on glass have been formed by the use of selenopolythionates. A solution of selenopolythionates was prepared from 0.4 mol/L H<sub>2</sub>SeO<sub>3</sub> and 1 mol/L NaHSO<sub>3</sub> 1:1 mixture. The components of H<sub>2</sub>SeO<sub>3</sub> and NaHSO<sub>3</sub> mixture react with each other and diseleniumtetrathionate acid in solution according to reaction is formed [4]:

 $2H_2SeO_3 + 5NaHSO_3 \rightarrow H_2Se_2S_2O_6 + Na_2SO_4 + NaHSO_4 + 3H_2O_3$ 

By heating  $H_2Se_2S_2O_6$  decomposes and releases elemental selenium, which is deposited on glass substrate:  $Se_2S_2O_6^{2-} \rightarrow Se + SeS_2O_6^{2-}$ 

Dark red colored Se film was deposited on glass substrate for 3 h at 60 °C. For the formation of copper selenide film the selenized sample was treated with 0.4 M Cu(II/I) salt solution at 60 °C for 10 min. Elemental selenium reacts with Cu(I) ions and forms copper selenide, Cu<sub>x</sub>Se:

 $Se + 2xCu^+ \rightarrow Cu_xSe + xCu^{2+}$ 

The formation of films was repeated three times. Obtained selenide films composition and the surface morphology were investigated by SEM-EDS analysis using a Quantax 400 from Bruker. With scanning electron microscopy, the irregular, dendritic copper selenide surface microstructure was determined. Energy dispersive spectroscopy was used to determine the chemical composition of the obtained layers. EDS shows the presence of Cu, Se and Si peaks.

1			
Cycle No	1	2	3
Cu, at. %	$24.73\pm0.7$	$24.12\pm0.7$	$27.55\pm0.9$
Se, at. %	$42.54 \pm 1.7$	$72.46 \pm 2.7$	$71.80 \pm 3.0$

Table. Elemental composition of obtained films (except Si)

The results indicate that films are rich in selenium (42.54 - 72.46 at.%). The highest amount of copper was in the sample obtained after three cycles.

#### References

1. B.M. Palve, V.S. Kadam, C.V. Jagtap, S.R. Jadkar, H.M. Pathan, J. Mater. Sci. Mater. Electron, 28 (2017) 14394-14401.

2. S. Thirumavalavan, K. Mani, S. Suresh, Chalcogenide Lett., 12 (2015) 237-246.

3. A. Zyoud, K. Murtada, H. Kwon, H.-J. Choi, T. W. Kim, M. H. S. Helal, M. Faroun, H. Bsharat, D. H. Park, H. S. Hilal, Solid State Sciences, 75 (2018) 53-62.

4. V. Zelionkaitė, A. Žarnauskas, Chem. Technol., 18 (2001) 56-60.

## THE CARBAZOLE AND TRIPHENYLAMINE MOIETIES-BASED SEMICONDUCTORS FOR GLUCOSE BIOSENSORS

Š. Žukauskas<sup>1</sup>, D. Palinauskas<sup>1</sup>, A. Ramanavičius<sup>1,2</sup>, <u>G. Bagdžiūnas<sup>1,2\*</sup></u>

<sup>1</sup>Department of Physical Chemistry, Vilnius University, Faculty of Chemistry and Geosciences, Naugarduko str. 24, Vilnius, Lithuania <sup>2</sup>Department of Material Science and Electrical Engineering, Center for Physical Sciences and Technology, Sauletekio av. 3, Lithuania \*Corresponding author, e-mail: gintautas.bagdziunas@ftmc.lt

Organic semiconductors are among the most promising next generation materials for biosensors as the greener and cheaper alternative to transition metal-based electrodes [1]. This communication focuses on the production and analysis of organic p-type semiconductor-based glucose biosensors. The compressed graphite electrodes have been electrochemically modified with 9-ethyl-9*H*-carbazole (CzEt), 9-phenyl-9*H*-carbazole (CzPh), N,N,N-triphenylamine (TPA) and cross-linked with glucose oxidase (GOx; EC 1.1.3.4).



Reaction of the created biosensors to the changing concentration of glucose has been assessed by cyclic voltammetry. The resulting sensors appear to display a linear range of analyte detection from 0.5 M to 5 M at the positive potential of +0.15 V vs Ag/AgCl and the highest sensitivity of 13.6  $\mu$ A cm<sup>-2</sup> mM<sup>-1</sup> for the CzPh-modified electrode. Herein, we aim at drawing the picture of the electro-polymerized derivatives and expect to motivate the scientific community to take into account applicability of p-type organic semiconductors for amperometric biosensors.

## Acknowledgments

Financial support from the Research Council of Lithuania a grant No. 09.3.3-LMT-K-712-02-0186 is gratefully acknowledged.

## References

1. G. Bagdžiūnas, Š. Žukauskas, A. Ramanavičius, Insights into a Hole Transfer Mechanism between Glucose Oxidase and a p-type Organic Semiconductor, *Biosensors and Bioelectronics*. 102 (2017) 449-455.

## ELECTROCATALYTIC AND PSEUDOCAPACITIVE PROPERTIES OF LAYERED NICKEL-COBALT OXIDE COATINGS ON STAINLESS STEEL

#### I. Barauskienė\*, E. Valatka

## Kaunas University of Technology, Radvilėnų str. 19, 50254 Kaunas, Lithuania \*e-mail: <u>ieva.barauskiene@ktu.lt</u>

Water electrolysis using renewable sources of energy (wind, solar, hydropower) generates high-purity (>99.999 %) hydrogen and is feasible on small and large scales [1,2]. The oxygen evolution reaction (OER) is responsible for kinetically sluggish process usually requiring high overpotential to form oxygen–oxygen bond [3]. Therefore, an effective catalyst is needed stabilizing the intermediate products of the OER. Transition metal-based peroxo- or oxo- species, especially containing nickel and cobalt, are reasonable choice due to their good photocatalytic and electrocatalytic activity, stability in alkaline solutions and earth abundant nature [4,5]. On the other hand, nickel and cobalt oxide compounds having layered structure with large interlayer spacing also distinguish with great pseudocapacitive properties. These kinds of materials are able to store energy by charge transfer between electrode and electrolyte due to the Faradaic reactions, occurring on the surface of active material [6,7].

As forming a 3D structure of the active material on a conductive support increase its electrocatalytic activity, a mechanically and chemically stable stainless steel mesh *Bekipor ST 20AL3* was chosen for this application. Small fiber diameter ( $d = 2-30 \mu m$ ), density and thickness (0.51 mm) of this mesh enable to increase the surface area along with the good accessibility of deeper filaments and free–flow of the electrolyte solution.

The aim of the present work was to prepare layered nickel-cobalt oxide films on *Bekipor ST 20AL3* mesh and to investigate their structure, electrocatalytic and pseudocapacitive properties. The structure of all as-deposited and annealed coatings was investigated by XRD, TG-DSC, AAS, Raman spectroscopy, SEM and EDX techniques.

Layered nickel–cobalt oxide coatings on *Bekipor ST 20AL3* mesh were potentiostatically electrodeposited using nitrate bath. Structure analysis revealed that as–deposited coatings consist predominantly of  $\alpha$ –Co(OH)<sub>2</sub> and  $\alpha$ –Ni(OH)<sub>2</sub> phases, which forms a spinel–type NiCo<sub>2</sub>O<sub>4</sub> structure after annealing at 473–673 K. It was established that the presence of spinel–type NiCo<sub>2</sub>O<sub>4</sub> phase results in a high activity of coatings in oxygen evolution reaction. Layered nickel-cobalt hydroxide coatings on *Bekipor ST 20AL3* were annealed applying five different temperatures: 473, 573, 673, 773 and 1073 K. Nickel–cobalt oxide, obtained after thermal treatment at 673 K, showed the best electrocatalytic activity. The galvanostatic charge–discharge measurements revealed that the best value of specific capacitance is 769 F·g<sup>-1</sup>. The presented results are relevant for practical application of earth–abundant metal (hydro)oxides in water anodic oxidation and charge storage devices. The prepared oxide materials were found to be promising candidates for the replacement of the most active, but high-cost and rare ruthenium and iridium compounds.

- 1. R. Kothari, D. Buddhi, R. L. Sawhney, Renew. Sust. Energ. Rev., 12 (2008) 553-563.
- 2. J. D. Holladay, J. Hu, D. L. King, Y. Wang, Catal. Today, 139 (2009) 244-260.
- 3. Y. Cheng, S. P. Jiang, Prog. Nat. Sci.-Mater., 25 (2015) 545-553.
- 4. A. Fernando, J. Phys. Chem. C, **119** (2015) 11072-11085.
- 5. H. S. Ahn, J. Yano, T. D. Tilley, ACS Catal., 5 (2015) 2573-2576.
- 6. C. D. Lokhande, D. P. Dubal, O. S. Joo, Curr. Appl. Phys. 11 (2011) 255-270.
- 7. H. Chen, T. N. Cong, W. Yang, C. Tan, Y. Li, Y. Ding, Prog. Nat. Sci. 19 (2009) 291-312.

## EXPERIMENTAL STUDY OF As(V) ADSORPTION ONTO DIFFERENT ADSORBENTS

## <sup>a</sup>Z. Danková, <sup>a</sup>A. Bekényiová, <sup>a</sup>Z. Bujňáková, <sup>b</sup>Z. Mitroová, <sup>a</sup>D. Gešperová, <sup>c</sup>I. Štyriaková, <sup>d</sup>D. Štyriaková, <sup>a</sup>J. Briančin

<sup>a</sup>Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 040 01 Košice, Slovakia <sup>b</sup>Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovakia <sup>c</sup>State Geological Institute of Dionýz Štúr, Regional center Košice, Jesenského 8, 040 01 Košice, Slovakia <sup>d</sup>Faculty of Mining, Ecology, Process Control and Geotechnologies, Technical University of Košice, Park Komenského 15, 042 00 Košice, Slovakia

Subsequent toxic elements contamination of soils is one of the main environmental problems of urbanization and industrialization and has recently become a serious concern in the world. Previous experiments have brought the new ecological way of contaminated soil treatment – biological-chemical leaching (extracting of toxic elements to the solution), but also the question of as obtained leachates processing. The reverse immobilization of toxic elements, e.g. Cu(II), Zn(II), As(V) from the water environment after the bioleaching process could be realized by adsorption and precipitation onto selected mineral materials and synthetic adsorbents. For this reason, the As(V) adsorption onto natural bentonite (B), Fe enriched bentonite (FeB) and synthetic magnetic particles (MP) from the aqueous solutions was investigated by batch tests as well as in column tests. The natural materials did not perform so good adsorption properties towards As(V) in the batch experiments as MP, which Q<sub>max</sub> was calculated for 18 mg/g. However in column experiments adsorption effect of natural materials was comparable with MP. After the percolation of the model solution through the columns filled with B and FeB sample decreased the As(V) concentration from 30 mg/L to lower than 2 mg/L. After the first cycle of percolation, both samples were effective in the second cycle with the same result. Solution containing 30 mg As(V)/L in the first cycle and 50 mg As(V)/L in the second cycle was percolated through the columns filled with FeB/MP layer and MP layer with quartz sand (OS). After both cycles the As(V) concentration decreased again below 2 mg/L. The third series of columns were filled with FeB/MP/QS and B/MP/QS. Two cycles with solution of 100 mg As(V)/L were performed. After the second cycle 73 % and 99 % of As(V) was removed by FeB/MP/QS and B/MP/QS, respectively. The first experimental study showed that natural materials should be used effectively as column fillers to fix finer magnetic particles. On the other hand, their selectivity towards Cu(II) and Zn(II) ions could be beneficial for regeneration of media used in the process of soil bioremediation.

Keywords: arsenic, bentonite, Fe-bentonite, magnetic particles

## Acknowledgement

This work was supported by the Grant Agency of the Slovak Republic VEGA Agency, Project No. 2/0049/15.

## SYNTHESIS OF GOLD NANOPARTICLES USING REDUCING SUGARS

**<u>B. Brasiunas</u><sup>1,2</sup>, A. Popov<sup>1,2</sup>, A. Ramanaviciene<sup>1,2</sup>** 

<sup>1</sup>NanoTechnas - Center of Nanotechnology and Materials Science, Institute of Chemistry, Faculty of Chemistry and Geosciences, Vilnius University, LT-03225, Lithuania <sup>2</sup>Department of Analytical and Environmental Chemistry, Vilnius University, Lithuania \*B. Brasiunas, e-mail: <u>benas.brasiunas@gmail.com</u>

Gold nanoparticles (AuNPs) have been widely employed in a range of biomedical applications due to their unique optical properties and multiple surface functionalities [1]. Properties of AuNPs depend on various parameters such as size, shape and the modification of the surface. A selection of synthesis method and conditions allows to obtain AuNPs with set of necessary properties [2]. Generally, AuNPs are synthesized by a chemical reduction method and toxic chemicals are used or contaminants are occasionally produced [3]. Enzymatic and biogenic syntheses can be used as an environment-friendly methods for AuNPs preparation and enlargement [4,5]. The usage of eco-friendly and readily available chemical substances allows to reduce the cost of synthesis and the impact on environment.

The main aim of this study was to employ various reducing sugars for AuNPs preparation. Glucose, fructose, mannose and lactose were used as the reducing agent. Synthesis of AuNPs was performed in a basic medium at room temperature where tetrachlorauric acid was used as a precursor for AuNPs, reducing sugars as a reducing agent and cetyltrimethylammonium bromide (CTAB) as a stabilizing agent. AuCl<sub>4</sub><sup>-</sup> ions are reduced to Au<sup>0</sup> creating AuNPs due to the oxidation of sugar in basic condition. The formation of AuNPs was evaluated using UV-Vis absorption spectroscopy method. Optimal concentrations of HAuCl<sub>4</sub>, NaOH and CTAB were determined for a sufficiently rapid preparation of stable AuNPs colloidal solution. Furthermore, the dependence of AuNPs formation speed on the type of reducing sugar was investigated. Dynamic light scattering, SEM and TEM methods were used for the characterization of AuNPs size. Replacement of CTAB by other eco-friendly stabilizing agents will improve environmental friendliness of the presented synthesis method.

- 1. Y. C. Yeh, B. Creran, V. M. Rotello, Nanoscale., 4 (2012) 1871–1880.
- 2. M. Sengania, A. M. Grumezescub, V. D. Rajeswari, OpenNano, 2 (2017) 37-46.
- 3. M. Nadeem, B. H. Abbasi, M. Younas, W. Ahmad, T. Khan, Green Chem Lett Rev, 10 (2017) 216-227.
- 4. A. Ramanaviciene, J. Voronovic, A. Popov, R. Drevinskas, A. Kausaite-Minkstimiene, A. Ramanavicius, Colloids Surf. A Physicochem Eng Asp, **510** (2016), 183–189.
- 5. S. Menon, S. Rajeshkumar, K. Venkat, Resource-Efficient Technologies, **3** (2017) 516-527.

## USE OF LA-ICP-MS AND IRMS DATA TO DISTINGUISH BETWEEN ORGANICALLY AND CONVENTIONALLY GROWN WHEAT

## L. Buša<sup>1,\*</sup>, L. Kępa<sup>2</sup>, A. Vīksna<sup>1</sup>, E. Bulska<sup>2</sup>

<sup>1</sup>University of Latvia, Faculty of Chemistry, Jelgavas 1, LV-1004, Riga, Latvia <sup>2</sup>University of Warsaw Biological and Chemical Research Centre, Żwirki i Wigury 101, 02-089, Warsaw, Poland

## \*Corresponding author, e-mail: <u>lauma.busa@lu.lv</u>

The total organic production of wheat and spelt in EU is growing by year. Consumers often prefer biologically grown food as it is considered to be healthier, safer and environmentally friendlier than the conventionally grown products. The revenue from organic product sales in 2015 in EU was 29.8 billion euros and is expected to grow to 34 billion in 2020 [1]. However, the superiority of organic wheat nutritional value has not been scientifically proven [2]. Additionally, the intensification of the organic sector and the higher prices of the organic products can be a cause for illegal activities – such as marketing of 'fake' organic products that haven't been grown according to the standards of organic farming. Therefore, it is needed to search for new authentication procedures and use novel analytical techniques [3].

Five varieties of wheat (*Triticum aestivum L.*) that have been grown organically and conventionally at the Institute of Agricultural Resources and Economics, Stende Research Centre were analyzed in order to establish the localization of various metallic elements in the grains and to evaluate their possible use as indicators for authenticity assessment. The analysis was carried out using LA-ICP-MS system with following laser (Laser LX-213 (CETAC); wavelength: 213 nm; spot size: 50  $\mu$ m; laser frequency: 20 Hz; scan rate: 20  $\mu$ m·s<sup>-1</sup>; 3 parallel lines) and ICP-MS (NexION 300D (PerkinElmer); RF power: 1350 W; nebulizer gas flow: 0.9 L·min<sup>-1</sup>; auxiliary gas flow: 1.2 L·min<sup>-1</sup>; plasma gas flow: 18 L·min<sup>-1</sup>) instrument settings. Altogether 13 metallic elements were determined (Na, Mg, Al, K, Ca, Mn, Fe, Cu, Zn, Rb, Sr, Mo, Ba). Additionally, carbon and nitrogen stable isotope ratios in whole grain flour, prepared from the samples, were measured using continuous flow EA-IRMS system Nu-Horizon (Nu Instruments).

The results have shown that in both organically and conventionally grown samples the metallic elements are mainly located in the germ, with very little amounts of the elements located in endosperm. Laser ablation followed by inductively coupled plasma mass spectrometry is a promising method to be used for authentication of biologically grown wheat. By combining the concentrations and localization of metallic elements in wheat grains with nitrogen stable isotope ratio values, a new methodology for organically grown food authentication could be elaborated.

- 1. Technavio, Organic Food and Beverages Market in Europe 2016-2020, 2016.
- 2. G. Langenkämper, C. Zörb, M. Seifert, P. Mäder, B. Fretzdorff, T. Betsche, J. Appl. Bot. Food Qual., 80 (2012) 150-154.
- 3. K.H.Laursen, A.Mihailova, S.D.Kelly, V.N.Epov, S.Bérail, J.K.Schjoerring, O.F.X.Donard, E.H.Larsen, N.Pedentchouk, A.D.Marca-Bell, U.Halekoh, J.E.Olesen, S.Husted, Food Chem., **141**(2013) 2812-2820.

## INVESTIGATION OF RED BALLPOINT PEN INKS

<u>A. Čiuladienė</u>\*, A. Luckutė, A. Kareiva

Department of Inorganic Chemistry, Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko st. 24, LT- 03225 Vilnius, Lithuania \*<u>ausra.ciuladiene@chgf.stud.vu.lt</u>

All the times people wanted to leave their trail for a future generation, so they wrote, painted and created different types of artworks. This has led to finding new pigments and inks. The history of modern writing instruments that we can find in each store began in the 20th century [1].

Document dating and the time that a document and/or ink could have been once placed on the paper is one of the most difficult and hardest problem for the restoration and conservation scientists. Basically, ink is usually a complex homogeneous medium, composed of solvents, pigments, dyes, resins, lubricants, solubilizers, surfactants, particulate matter, fluorescers and other materials. This mixture of components, usually under patent, is useful for giving the colour, controlling density or flow, modifying the drying kinetic and providing the final appearance [2, 3].

The aim of this work was to characterize three different red ballpoint pen *Bic, Forpus* and *Centrum* inks using SEM-EDX analysis, ATR-FTIR spectroscopy, TG/DTG analysis and UV-Vis spectroscopy.

Keywords: Red inks, SEM-EDX, ATR-FTIR, TG/DTG, UV-Vis

- 1. O. Díaz-Santana, F. Conde-Hardisson, D. Vega-Moreno, Microchemical Journal., **138** (2018) 550-561.
- 2. <u>M. Ezcurra, J. M.G.Góngora, I. Maguregui, R. Alonso</u>, Forensic Science International., **197**, (2010) 1-20.
- 3. M. Calcerrada, C. García-Ruiz, Analytica Chimica Acta., 853 (2015) 143-166.

## SOLAR AIR THERMAL COLLECTORS FOR APPLICATION IN THE FOOD INDUSTRY

## O. Demchyna<sup>1</sup>, B. Rachiy<sup>2</sup>, A. Kostruba<sup>3</sup>, L. Romanyuk<sup>4</sup>, V. Bahriychuk<sup>5</sup>, R. Romanyuk<sup>6</sup>, R. Musiy<sup>1,\*</sup>

<sup>1</sup>Department of Physical Chemistry of Fossil Fuels InPOCC, National Academy of Sciences of Ukraine, 3a Naukova Str, Lviv, 79053, Ukraine

<sup>2</sup>Vasyl Stefanyk Precarpathian National University, 57 Shevchenko Str., Ivano-Frankivsk,

<sup>3</sup>Lviv University of Commerce and Economic, 9 Samtshuk Str., Lviv, Ukraine

<sup>4</sup>Ecological College of Lviv National Agrarian University, 167 Zamarstynivska Str., Lviv, <sup>5</sup>The Company

"Kartekiya-Build", Ternopil, Ukraine

<sup>6</sup>Western Scientific Center of the National Academy of Sciences of Ukraine and the Ministry of Education and Science of Ukraine, 4 Mateyka Str., Lviv, Ukraine

\*Corresponding author, e-mail: <u>rostyslav\_musiy@ukr.net</u>

In the food industry, the main task of manufacturers is to maximize the preservation of useful properties of products. An important role in this process is played by the technology of processing vegetables and fruits.

There are different ways to store foods and preserve their nutritional properties:

- creation of controlled storage conditions in fruit and vegetable stores;

- treatment of products with high temperatures or freezing in freezers;

- saturation of products from preservatives (sugar, artificial chemical compounds, products of combustion of organic fuel, etc.);

- evacuation, fermentation, dehydration and others.

However, they all need expensive equipment and high energy costs.

One of the most common methods of canning is drying. It is simple and convenient. Dried fruits and vegetables under optimum conditions can be stored for more than one year, and in sealed containers - even longer. They are more nutritious and calorie.

For this purpose, we have designed ecologically clean dryers based on solar air thermal collectors (Photo 1). Solar collectors [1-3] work exclusively on solar energy. They blow through the dryer environmentally clean warm air, do not contaminate food and the environment. Dryers are made from special varieties of wood that do not smell. Dryer designs are very simple and easy. They provide a very simple installation, have the opportunity to put in a garden, vegetable garden, on any locality and indoors..

The person does not bear any expenses and additional payments for maintenance during its operation. In addition, the device is switched on and off automatically when there is a sun. This is very convenient because it does not require human presence while working.



Photo 1. A dryer based on the solar air heat collector.

- 1. Orozbaiev, M.T. (2007). To the definition of thermal technical characteristics of flat solar air-heating collectors. Heliotekhnika, 1, 81-83.
- 2. Zavadska, M. (2003). Solar Collectors, Heat Pumps. Na Tak Warsaw: Polska Ekologia, 276 p.
- 3. Sergii Khairnasov, Boris Rassamakin, Andrii Rassamakin, Rostyslav Musiy . Journal of Civil Engineering and Architecture, Volume 7, No. 4 (Serial No. 65), April **2013**, pp. 403-409.

## FIXING OF Nd(III) IONS ON THE SURFACE OF MONO- AND BIFUNCTIONAL SILICA SBA-15 TYPE TO PROVIDE THEM LUMINESCENT PROPERTIES

#### V.V. Sliesarenko, O.A. Dudarko\*, I.V. Melnyk

*Chuiko Institute of Surface Chemistry of NAS of Ukraine, Generala Naumova 17, 03164 Kyiv, Ukraine* \*Corresponding author, e-mail:odudarko80@gmail.com

Lanthanides can form complex compounds with P-containing functional groups. The advantage of lanthanide coordination compounds compared with complexes of s-, p-, and d-metals is that lanthanide ions are characterized by narrow-band luminescence in a wide spectral range, which is due to transitions between 4f-sublevels and long lifetime of the excited states. So, this work is dedicate to obtaining SBA-15 silica with phosponic groups and Nd (III) adsorption to create luminescent composite. Firstly  $-PO(OH)_2$  were fixed to a matrix of SBA-15 type mesoporous silica by a direct method [1]. Since water molecules have the ability to reduce luminescence, for this reason, half of the functional groups  $-PO(OH)_2$  were replaced by the hydrophobic -SH groups [2]. As can be seen from Fig. 1 the bifunctional sample is inferior to the monofunctional sample due to Nd (III) sorption capacity. The phosphonic groups are less densely distributed on the surface of bifunctional sample than on the monofunctional and it could also be affected the ratio functional group:Nd (for SBA/PO(OH)<sub>2</sub> was 1:2.59, and for SBA/PO(OH)<sub>2</sub>/SH - 1:3.75). Accordingly, it can be concluded that thiol groups affect the processes of complexation on the surface.



Fig.1. Adsorption isotherms

The work was carried out with the financial support of the joint Ukrainian-Lithuanian research project M/65-2018.

- 1. Dudarko O., Zub Y. Chem. J. of Moldova. Gen., Ind. and Ecol. Chem., 12(2), (2017) 79-86.
- 2. Dudarko O. A., Tomin O. O., Tomina V. V., Sliesarenko V. V., Zub Yu. L. J. Pharm. Appl. Chem., 3(3), (2017) 177-183.

## PHOSPHOLIPID BILAYER FORMATION ON FLUORINE DOPED TIN OXIDE

## I. Gabriunaite<sup>1\*</sup>, A. Valiūnienė<sup>1</sup>

Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko Str. 24, LT- 03225, Vilnius, Lithuania \*Corresponding author, e-mail: inga.gabriunaite@chf.vu.lt

Phospholipid bilayer is widely investigated structure. Over the years, membrane formation on gold surfaces has improved massively and research had shown great results, especially in the field of toxin detection [1]. But as any other system it has some flaws. Firstly, the cost to produce sputtered gold films is really high. Secondly, self – assembled monolayer (SAM) of alkanethiols on gold over long term exposure to water leads to forming SAM islands, which are not very suitable for phospholipid bilayer formation [2].

In this paper is proposed a new system to form phospholipid bilayer. As substrate was used thin film metal oxide – fluorine doped tin oxide (FTO). Mainly because it is a lot more cheaper than gold and materials required to produce it are more abundant in the environment. For monolayer formation it was chosen silane based materials, which during SAM formation undergoes hydrolysis reaction. Finally a stable chemical bond is formed. Such monolayer is very stable and suitable phospholipid membrane formation multiple times.

To summarize, presented system is suitable for phospholipid bilayer formation. Moreover, it could be applied for various membrane proteins investigations, such as toxins or electron transfer proteins.

- 1. G. Valincius, M. Mickevicius, T. Penkauskas, M. Jankunec, Electrochim. Acta, 222 (2016), 904–913.
- 2. B. Rakovska, T. Ragaliauskas, M. Mickevicius, M. Jankunec, G. Niaura, D. J. Vanderah, G. Valincius, Langmuir, 31 (2015) 846.

## LASER-INDUCED REDUCTION OF GRAPHENE OXIDE-DYE NANOCOMPOSITES: THE EFFECT OF DYE MOLECULES ON GRAPHENE SHEETS QUALITY AND STRUCTURAL PROPERTIES

## J. Gaidukevič<sup>1,\*</sup>, R. Trusovas<sup>2</sup>, G. Niaura<sup>2</sup>, I. Mališauskaitė<sup>1</sup>, J. Barkauskas<sup>1</sup>

<sup>1</sup>Vilnius University, Naugarduko str. 24, LT-03225 Vilnius, Lithuania <sup>2</sup>Center for Physical Sciences and Technology, Sauletekio av. 3, LT-10257 Vilnius, Lithuania \*Corresponding author, e-mail: <u>justina.gaidukevic@chf.vu.lt</u>

Graphene could be widely employed in the specific fields such as optoelectronics, medicine bioscience, catalysis-chemistry, and electrochemical energy storage, which is due to its unique properties [1]. One of the most promising method to produce graphene in large scale is based on the reduction of GO to graphene. Thermal and chemical reduction are the most frequently used processes for the removal of oxygen-containing groups. However, during the thermal reduction a large number of defects that deteriorate the electrical properties of graphene are created, while the chemical reduction includes the use of hazardous aggressive materials [2]. Recently, it has been demonstrated that GO can be reduced using laser-irradiation [3]. Nevertheless, the experts emphasize that to produce low-defect graphene using laser irradiation require a precise control of laser parameters. The use of short laser pulses might be beneficial for this process. The carbon-rich precursor used in laser-scribing process is one more important factor to prepare a high-quality rGO coating [4]. Despite the great progress in the field of laser-induced graphene production, the process is still at its infancy and many challenges are to be resolved.

The aim of this work was to prepare graphene-dye nanocomposite coatings, perform their reduction applying laser irradiation and to investigate structural properties.

Graphene oxide (GO) was prepared from the natural graphite by the synthesis protocol reported by Yan et al. [5]. Obtained brown powder was dried and used for the fabrication of GO and GO-Dye coatings. Six dyes (Acridine yellow, Neutral red, Malachite green, Auramine O, Congo red and Evans blue) from three different classes (Acridine, Arylmethane and Diazo) were used for the preparation of nanocomposite coatings. Two series of coatings with dye concentration of 5.0 wt% and 20.0 wt% have been made. The obtained coatings were treated using the picosecond laser (Atlantic, 10 ps, 100 kHz, Ekspla) working at the 1064 nm. Prepared samples were tested by different methods (Raman and FTIR spectroscopy, contact angle measurements, TG analysis).

The results show that the level of GO reduction to graphene phase dependent on the structure of a dye (as well as the concentration of a dye) used for the preparation of a nanocomposite.

#### Acknowledgments

This research is funded by Lithuanian Research Council via measure "Towards Future Technologies", Project No. LAT 11/2016.

- 1. M. J. Allen, V. C. Tung, R. B. Kaner, Chem. Rev., 110 (2010) 132–145.
- 2. S. A. Bhuyan, N. Uddin, M. Islam, F. A. Bipasha, S. S. Hossain, Int. Nano. Lett., 6 (2016) 65–83.
- 3. R. Trusovas, G. Račiukaitis, G. Niaura, J. Barkauskas, G. Valušis, R. Pauliukaite, Adv. Optical Mater., 4 (2016) 37.
- 4. Y. Zhao, Q. Han, Z. Cheng, L. Jiang, L. Qu, Nano Today 12 (2017) 14-30.
- 5. X. Yan, J. Chen, J. Yang, Q. Xue and P. Miele, App. Mater., 9 (2010) 2521-2529.

## DEVELOPMENT OF A NOVEL AMPEROMETRIC GLUCOSE BIOSENSOR BASED ON GLUCOSE OXIDASE FUNCTIONALIZED POLY(PYRROLE-2-CARBOXYLIC ACID) PARTICLES

## L. Glumbokaite<sup>1</sup>, E. Dauksaite<sup>1</sup>, A. Kausaite-Minkstimiene<sup>1,\*</sup>

<sup>1</sup> NanoTechnas – Centre of Nanotechnology and Material Science, Institute of Chemistry, Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko str. 24, LT-03225 Vilnius, Lithuania \* Corresponding author, e-mail: asta.kausaite@chf.vu.lt

Nowadays the importance and need of sustainable, long lasting, environment-friendly devices are seen in many fields. Development of simple and low cost medical devices such as blood glucose sensors are not an exception [1]. Researches are constantly seeking for materials and technologies that would help to develop sensitive, selective and reliable glucose biosensors. Conjugated polymers (CP) provide many new opportunities in this area. Due to unique properties, such as compatibility with biological molecules in neutral aqueous solutions, simple synthesis, high environmental stability and electrical conductivity these materials have numerous practical applications in biosensors [2], biomedical devices [3], enzyme immobilization matrices [4] or drug delivery [5]. Polypyrrole (PPy) has been one of the most widely studied CP during the past decade. In the development of biosensors, Ppy has been used as relatively stable and porous matrix for enzyme immobilization, which is ideally permeable to the analyte, but restrict the passage of larger molecules such as immobilized enzyme or electron transfer mediator. We designed and investigated a novel amperometric glucose biosensor based on graphite rod (GR) working electrode modified with glucose oxidase (GOx) functionalized poly(pyrrole-2-carboxylic acid) (PCPy) particles (GR/PCPy-GOx), which were synthesized by chemical oxidative polymerization technique as described in our previous publication [6]. Carboxylic groups located on the PCPy particles surface provide the possibility of covalent immobilization of enzyme. The amperometric responses of designed glucose biosensor were obtained at different concentrations of glucose and a certain amount of phenazine methosulfate (PMS, PMSH<sub>2</sub> – reduced form of PMS), which was used as electron transfer mediator (Fig. 1). Covalent immobilization of the GOx has created a stable enzyme layer on electrode surface and enhanced performance of the biosensor.



Fig 1. Operation's illustration of designed amperometric glucose biosensor.

- 1. A. Márquez, C. Jiménez-Jorquera, C. Domínguez, X. Muñoz-Berbel, Biosensors and Bioelectronics, 97 (2017) 136-142.
- 2. J. Wang, M. Musameh, Analytica Chimica Acta, 539 (2005) 209-213.
- 3. A. D. Bendrea, L. Cianga, I. Cianga, Journal of Biomaterials Applications, 26 (2011), 3-84.
- 4. H. H. Ciftci, Y. Oztekin, U. Tamer, A. Ramanaviciene, A. Ramanavicius, Colloids and Surfaces B: Biointerfaces, **123** (2014) 685-691.
- J. A. Chikar, J. L. Hendricks, S. M. Richardson-Burns, Y. Raphael, B. E. Pfingst, D. C. Martin, Biomaterials, 33 (2012) 1982-1990.
- A. Kausaite-Minkstimiene, A. Ramanaviciene, R. Simanaityte, D. Gabrielaitis, L. Glumbokaite, A. Ramanavicius, RSC Advances, 127 (2015) 105475-105483.

## STABILITY OF BIOMASS-BASED LEVOGLUCOSENONE IN AQUEOUS SOLUTIONS

D. Godina<sup>1,2\*</sup>, K. Meile<sup>1,2</sup>, A. Zhurinsh<sup>1</sup>, R. Pomilovskis<sup>1</sup>

<sup>1</sup>Latvian State Institute of Wood Chemistry, Dzerbenes 27, LV-1006 Riga, Latvia <sup>2</sup>University of Latvia, Jelgavas 1, LV-1004 Riga, Latvia \*danielagodina393@gmail.com

Biomass is a valuable renewable resource, which can be used to produce not only heat and energy, but also materials and chemicals. A well-established processing method of biomass is pyrolysis or thermal degradation in the absence of oxygen. Levoglucosenone (LGO) is best obtained by the depolymerization and dehydration of cellulose in the process of catalytic pyrolysis at comparatively low temperatures. [1]. The LGO molecule is an appealing starting material for the synthesis of "green" solvents, such as dihydrolevoglucosenone [2].

In pyrolysis products LGO is most often determined by gas chromatography with flame ionization detector or mass spectrometry, but high-performance liquid chromatography (HPLC) has also been described in literature [3]. For the determination of LGO reversed phase HPLC is usually used with aqueous mobile phases, so the aim of this work is to evaluate the stability of LGO in aqueous solutions. Knowledge about the degradation trends of LGO in aqueous solutions is important for storage, sample preparation and analysis of pyrolysis products.

In this study LGO was determined by reversed phase UHPLC-UV with a mobile phase consisting of a mixture of water and acetonitrile, so the stability of LGO solutions in water and a water/acetonitrile (50:50) mixture was evaluated. The solutions of standard LGO, as well as a LGO containing sample of pyrolysis products were stored at 5 °C and 21 °C ( $\pm$  1 °C) temperature for three months and analyzed with intervals of several days. Fig. 1. shows, how the concentration of LGO standard in the solutions decreased with time. It was concluded, that LGO degradation is the fastest in the aqueous medium. This is due to the effect of water as a polar proton donor solvent. The acetonitrile additive slows the degradation rate of LGO. LGO degradation is also influenced by the storage temperature of the solution, at 21 °C the degradation is noticeably faster. Studies have also concluded that pH is a significant factor in the degradation of LGO - the acid acts as a catalyst and accelerates LGO degradation.



Fig. 1. The decrease of the concentration of LGO in different solvents at 5  $^\circ C$  and 21  $^\circ C$ 

The research was supported by the ERDF project No. 1.1.1/16/A/010 "Developing an innovative technology for producing levoglucosenone from lignocellulose".

- 1. X. Sui, Z. Wang, B. Liao, Y. Zhang, Q. Guo, *Bioresour. Technol.*,103(1), 466 (2012)
- 2. S.H. Krishna, D.J. McClelland, Q.A. Rashke, J.A. Dumesic, G.W. Huber. Green Chem., 19, 1278 (2017)
- 3. H. Kawamoto, W. Hatanaka, S. Saka, J. An. Appl. Pyrol., 70, 303 (2003)

## PREAPARATION OF POROUS GLASS-CERAMIC (GC) AND POLYMERIZED 1,6-HEXANEDIOL DIACRYLATE (HDDA) COMPOSITE USING FREE RADICAL COPOLYMER CROSSLINK REACTIONS AND BLOWING AGENT FOR BONE TISSUE ENGINEERING

## <u>R. Golubevas<sup>1</sup></u>, A. Žarkov<sup>2</sup>, L. Alinauskas<sup>1</sup>, A. Kareiva<sup>3</sup>, E. Garskaite<sup>1</sup>

<sup>1</sup>Department of Applied Chemistry, Institute of Chemistry, Faculty of Chemistry and Geoscience, Vilnius University, Naugarduko 24, Vilnius LT-03225, Lithuania

<sup>2</sup>Department of Analytical and Environmental Chemistry, Institute of Chemistry, Faculty of Chemistry and Geoscience, Vilnius University, Naugarduko 24, Vilnius LT-03225, Lithuania

<sup>3</sup>Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Chemistry and Geoscience, Vilnius University, Naugarduko 24, Vilnius LT-03225, Lithuania

Various acrylates are used as a common bone grafting material but mainly for the fixation as it doesn't has osteoconductive properties. The encapsulation of glass-caramics and formation of open pores into the composite subsequently alters the osteoconductive properties of the final product [1, 2]. The preparation of a glass-ceramic (GC)–polyhexandiol diacrylate (PHDDA) composite material is reported.

Precursor GC powders were synthesised via sol-gel method. The GC-PHDDA composite samples with different fractional GC content were prepared via photopolymerization reaction [3, 4].

1mg/L solution of Azodicarbonamide dissolved in DMF/DMSO in ratio 9:1 was used as a blowing agent. The formation of open pores on the surface of composites via polymerization reaction was observed. Cross section of composite has revealed presence of pores inside the composite.

The structures of the resultant surface were studied by ICP-OES, FE-SEM/EDX, FTIR and XRD techniques.

Keywords: glass-ceramic, PHDDA, sol-gel, FE-SEM, EDX, ICP-OES, bone tissue.

#### **References:**

[1] Ravarian, R., et al., RSC Advances, 2015, 5(75), 60681- 60690.

[2] Ravarian, R., et al., J. Mater. Chem. B, 2013, 1(13), 1835-1845

- [3] Charles E.Hoyle, et al., Polymer, 1988, Volume 29, Issue 1, 18-23.
- [4] Bull. Korean Chem. Soc. 2001, Vol. 22, No. 7 769.

## DEVELOPMENT OF TXRF METHOD FOR DETERMINATION OF CALCIUM AND PHOSPHORUS RATIO IN HYDROXYAPATITES

## V. Grebnevs<sup>1</sup>, A. Viksna<sup>1</sup>, O. Purmalis<sup>2</sup>, K. A. Gross<sup>3</sup>, L. Pluduma<sup>3</sup>

<sup>1</sup>Faculty of Chemistry, University of Latvia, Jelgavas street 1, Riga, Latvia <sup>2</sup>Faculty of Geography and Earth Sciences, University of Latvia, Jelgavas street 1, Riga, Latvia <sup>3</sup>Biomaterials Research Laboratory, Riga Technical University, P. Valdena street 3/7, Riga, Latvia *e-mail: vladgrebnev36@gmail.com* 

Hydroxyapatites and other calcium phosphates, being similar to a chemical structure of human bone inorganic constituents, nowadays are mostly recognized and widely used biomaterials for bone and teeth renewal. As any biomaterials, calcium phosphates are characterized by different parameters. From the analytical point of view, the underlying quantitative parameter is calcium and phosphorus (Ca/P) ratio. It has a fixed numerical value with a narrow allowable interval to fit in. Increased or decreased Ca/P ratio leads to severe deterioation of implant quality. These facts determine the need of strict Ca/P control using a simple and low-cost analytical procedure which would allow to measure Ca/P ratio quickly and precisely performing routine hydroxyapatite quality control.

Nowadays used methods (photometry, ICP-OES, gravimetry and other), being well-established and easily accessible, still have some essential limitations and difficulties in an effective introduction of them into routine analyses practice. Accordingly, elaboration of a new analytical method is an actual task. The data gathered in the course of continuous investigation of different Ca/P ratio determination methods in hydroxyapatites showed that TXRF (Total reflection X-ray spectrometry) is the most applicable method for this application due to relatively short one analysis time, possibility of a multi-element analysis to a fairly high degree of accuracy, low hardware maintenance costs and other advantages. Until now TXRF method has been successfully applied to different biological samples [1].

On the other hand, this method suffers from a number of limitations that referes to obtain precise quantification results for both elements. A key problem is a small sensitivity of phosphorus in X-ray analyses due to its relatively small atomic number. Other major drawback is difficulty in achieving uniform crystallization and distribution of sample containing elements applying analyzed solution on a carrier and drying the droplet.

Foreground aim of the research was to achieve as high as possible accuracy of calcium and phosphorus quantification results by TXRF method.

Table 1.

		0
Method	WCa	WP
Gravimetry	$39,810 \pm 0,009$	$18,471 \pm 0,015$
Photometry	$39,82 \pm 0,03$	$18,399 \pm 0,017$
Titrimetry	$39,83 \pm 0,07$	- <sup>a</sup>
ICP-OES	$39,78 \pm 0,02$	$18,44 \pm 0,03$
FAAS	$39,83 \pm 0,09$	- <sup>a</sup>
WD-XRF	$39,84 \pm 0,13$	$18,44 \pm 0,08$
TXRF	$39,78 \pm 0,02$	$18,402 \pm 0,018$

#### Calcium and phosphorus mass fraction (w, %) determination results using different analytical methods

<sup>a</sup>analysis was not performed and/or not possible

#### References

1. A. Viksna, E. Selin Lindgren, I. Kjellmer, J. Bursa. J. Trace and Microprobe Techniques., 4 (2002) 553-564.

## CHLOROPHYLL-A CONCENTRATION RETRIEVAL FROM SENTINEL-2 DATA IN LAKES IN LITHUANIA

D. Grendaitė<sup>1,\*</sup>, E. Stonevičius<sup>1</sup>, J. Karosienė<sup>2</sup>, K. Savadova<sup>2</sup>, J. Kasperovičienė<sup>2</sup>

<sup>1</sup>Hydrology and Climatology Department, Vilnius University, M. K. Čiurlionio str. 21/27, LT-03101 Vilnius,

Lithuania,

<sup>2</sup>Nature Research Center, Akademijos str. 2, Vilnius, LT-08412, Lithuania

\*dalia.grendaite@gmail.com

Inland waters are an important habitat for biota and are widely used for recreational needs and fishery. Water quality in eutrophic lakes can be affected by cyanobacteria blooms that pose a threat to lake ecosystems and people. *In situ* measurements carried out by the regional environmental protection agency's departments are time consuming and require considerable human and technical resources. Sentinel-2 satellites launched by the European Space Agency in relation to Copernicus project provide a continuous, free, high spatial (10-20 m) and temporal (3-5 days revisit time over the same point) resolution data than can be used to monitor lake water quality.

The aim of this study was to develop new algorithm for chlorophyll-a concentration retrieval in eutrophic lakes in Lithuania using the Sentinel-2 imagery. The pigment chlorophyll-a is an indicator of phytoplankton biomass and is often used for observation of the trophic state of the lake. We used *in situ* chlorophyll-a concentration data from 115 lakes in Lithuania. We grouped these lakes based on their spectral profiles using clustering analysis and focused on the group of eutrophic lakes. The scattering peak near 700 nm wavelength is a good indicator for phytoplankton biomass and chlorophyll-a concentration [1].

The most accurate ( $R^2 = 0.85$ ) empirical equation that we got (Fig. 1) was based on the reflectances in bands B4 and B5 of the Sentinel-2 Multispectral Imager:

 $Chla = 16.93 - 2154.27 \times B4 + 20.53.76 \times B5.$ 

The equation allowed us to calculate the chlorophyll-a concentration with 7.4  $\mu$ g L<sup>-1</sup> root mean squared error. With this equation we were able to estimate the trophic state of the lake (Trophic State Index) [2] correctly for the 77 % of lakes studied. The developed equation performed better than 18 other algorithms that we tested.

The derived empirical equation based on the Sentinel-2 imagery can be used for approximate chlorophyll-a concentration calculation and estimation of the trophic state of the lake. It could be used as a complementary tool to evaluate water quality in eutrophic lakes in Lithuania.

#### References

1. T. Kutser, B. Paavel, C. Verpoorter, M. Ligi, T. Soomets, K. Toming, G. Casal, Remote sensing of black lakes and using 810 nm reflectance peak for retrieving water quality parameters of optically complex waters. Remote Sensing (2016) 8(6): 497.

2. R. E. Carlson. A trophic state index for lakes. Limnology and oceanography (1977) 22(2): 361-369.



Fig. 1. The relationship graph between the in situ chlorophyll-a concentration and the chlorophyll-a concentration calculated by the derived empirical equation. The line indicates 1:1 line

## PREPARATION AND ANALYSES OF CERIUM DOPED YTTRIUM ALUMINIUM GARNET, BORON NITRIDE AND POLYMER COMPOSITES

G. Inkrataitė<sup>1</sup>, J. Aglinskaitė<sup>2</sup>, P. Vitta<sup>2</sup>, R. Skaudžius<sup>1</sup>

<sup>1</sup>Institute of Chemistry, Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania

<sup>2</sup>Institute of Photonics and Nanotechnology, Faculty of Physics, Vilnius University, Saulėtekio av. 3, LT-10257 Vilnius, Lithuania

e-mail: greta.inkrataite@chgf.stud.vu.lt

Cerium doped yttrium aluminum garnet is one of the most frequently used fluorescent materials. First studies on this material and its applications have been done as earl as year 1967 [1].However in the recent years research on this garnet has been revitalized, because of its use in the new generation of LED lighting. Even so, one of the main drawbacks of diodes is the problem of their lackluster lifespan. In order to improve longevity of the LEDs as well as the intensity of the emitted light, new research is focused on making new YAG:Ce composite materials as well as their integration into the diode itself [2]. Over the last few decades scientists have been trying to improve the luminescence intensity of phosphors. One way to do so is to use laser as an excitation source. However this makes phosphors heat up, and in order to prevent that measures need to be taken. Sometimes boron nitride is added together with the phosphor in order to improve thermal conductivity. In literature it is also reported that luminescence properties can be improved by addition of certain polymers [3].

For this project different composites were prepared, which could be used in LED in order to improve their longevity and reliability. For the reason, YAG:Ce phosphor powder was synthesized by sol-gel combustion method and then mixed together with differing amounts of BN and either M600 or M280 monomer which were polymerized under UV light. Composites were analyzed by x-ray diffraction (XRD), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). Also luminescence properties such as quantum efficiency, decay times, emission spectrum.

Acknowledgments. This work was financed by "Lietuvos mokslo taryba" in the frame of the project "Studentų gebėjimų ugdymas vykdant tyrimus semestrų metu". No. 09.3.3-LMT-K-712-10.

## Literature:

[1] Bachmann, V., C. Ronda, and A. Meijerink, Temperature Quenching of Yellow Ce3+ Luminescence in YAG:Ce. Chemistry of Materials, 2009. 21(10): p. 2077-2084

[2] Zhang, R., et al., A new-generation color converter for high-power white LED: transparent Ce3+:YAG phosphor-in-glass. Laser & Photonics Reviews, 2014. 8(1): p. 158-164.

[3] Wang, X., et al., Effect of Boron Nitride (BN) on Luminescent Properties of Y3Al5O12:Ce Phosphors and their White Light-Emitting Diode Characteristics. International Journal of Applied Ceramic Technology, 2012. **10**(4): p. 610-616.

## ENVIRONMENT FRIENDLY SORPTION-DIFFUSION METHOD FOR TIN SELENIDE LAYERS FORMATION

## R. Ivanauskas\*, A. Kunciūtė

Department of Physical and Inorganic Chemistry, Kaunas University of Technology, Radvilėnų Str., 19, LT-52254, Kaunas, Lithuania \*remigijus.ivanauskas@ktu.lt

A large amount of electrical energy are produced by burning organic fuel in thermal energy storages or using nuclear reaction in nuclear power plants. These sources of electrical energy associate with carbon dioxide emission and risk of radiation [1, 2]. Due to this it is very important to search more environment friendly methods for electrical energy generation: hydroelectric power station, wind power plants, solar cells [3].

Metal chalcogenides layers, such as cadmium selenide, lead selenide, tin selenide, are used in solar cells [4]. Tin selenide layers are valuable for their non-toxicity, semi-conductive properties (narrow optical band gap varying between 1.0 and 1.1 eV), low antireflection value and high absorption coefficient. High quality tin selenide layers can be formed by chemical vapor deposition method [5]. This method require sophisticated instruments and regular control, because unreacted chemical vapor can be eliminated into atmosphere. Also incorrect precursor selection increase risk of toxic products formation [6].

In this work tin selenide layers on hydrophilic polymer polyamide 6 surface were formed by simple and environmental friendly sorption-diffusion method. This method consists of two stage. In the first stage polyamide 6 sheets were treated with 0.1 mol/l selenotrithyonate in HCl 0.1 mol/l solution for 120 minutes at 60 °C temperature. In the second stage, seleniumized polyamide 6 sheets were immersed in different concentration tin (II) precursor solution for 60 minutes at 85 °C temperature. The surface morphology of these layers was analyzed by scanning electron microscope (SEM), elemental constitution was studied by energy-dispersive X-ray spectroscopy (EDX).

- 1. R. Sims, H. Rogner, Energy Policy, **31** (2003) 1315-1326.
- 2. H.G. Kim, T.Y. Kong, Radiation Protection Dosimetry, 146 (2011) 136-139.
- 3. Pochtovyuk, K. Pryakhina, Ekonomicznego we Wroclawiu, 502 (2018) 104-113.
- 4. S. Deo, A. Singh, Journal of Electronic Materials, 44 (2015) 4098-4127.
- 5. Z. Wang, F. Pang, Chemical Physics Letter, 702 (2018) 90-95.
- 6. Guide to Industrial Assessments for Pollution Prevention and Energy Efficiency, Ohio, 2001, p. 149.

## PECULIARITIES OF THE GALLIUM SELENIDE LAYERS FORMATION ON THE POLYAMIDE FILM SURFACE

#### V. Ulevičienė, <u>R. Ivanauskas</u>\*, L. Samardokas

Kaunas University of Technology Institution, Department of Physical and Inorganic Chemistry, Radvilenu str. 19, LT-50254 Kaunas, Lithuania \* E-mail: remigijus.ivanauskas@ktu.lt

Polymers modified by thin electrically conductive or semi conductive layers of binary inorganic compounds, particularly of metal chalcogenides represent a new class of materials – composites. Of particular interest are composite materials with binary selenides of III group metals. For example, GaSe is used as far-infrared conversion material [1],  $In_2Se_3$  – in optoelectronic devices [2] since, depending on the growth conditions and doping, it exhibits either n- or p-type conduction. In general, thallium selenides can be used for the production of photocells [3] and photoconductors [4]. Various physical methods were used for the formation of metal selenide layers on various dielectrics and on the polymers too: vacuum evaporation [5], flash evaporation [6], solid-state reaction [7] etc. The chemical deposition methods are low cost processes and the films are found to be of comparable quality to those obtained by more sophisticated and expensive physical deposition process [8].

In this work, using two stages sorption-diffusion method, gallium selenide layers were formed on semi hydrophilic polyamide PA 6 surface (70 mm thickness). In the first stage, polymer samples were seleniumized for 90 min in 0.05 mol·dm<sup>-3</sup> K<sub>2</sub>SeS<sub>2</sub>O<sub>6</sub> at pH 2.15, adjusted using 0.1 mol·dm<sup>-3</sup> HCl at 60 °C. In the second stage, seleniumized samples were treated in various concentration gallium sulfate salt solution for 30 min and 80 °C at various pH. The aim of this study was to investigate the influence of pH values and the concentration of gallium sulfate solution to the formation process and composition of gallium selenide layers on the PA film surface. The pH values of gallium sulfate solution were adjusted with potassium alkali or with concentrated solution of ammonia. Total amount of gallium and selenium in gallium selenide layers was determined using atomic absorption spectrophotometry.

#### 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.

#### References

1. J. Guo, J. J. Xie, D. J. Li, G. L. Yang, F. Chen, Ch. R. Wang, L. M. Zhang, Y. M Andreev, K. A. Kokh, G. V Lanskii and V. A Svetlichnyi, Light: Science & Applications (2015) 4, e362; doi:10.1038/lsa.2015.135

- R. Sreekumar, T.H. Sajeesh, T. Abe, Y. Kashiwaba, C. Sudha Kartha, K.P. Vijayakumar, Phys. Stat. Sol., 250 (2013) 95–102.
  P. S. Nayar, W. O. Hamilton, Appl. Opt., 16 (1977) 2942–2944.
- 4. S. A. Hussein, A. T. Nagat, N.M. Mohamed, Cryst. Res. Technol., 24 (1989) 685-692.

5. M. Kemmler, M. Lazell, P. O'Brien, D.J. Otway, J.-H. Park, J.R. Walsh, Journal of Materials Science: Materials in Electronics, 13 (2002) 531-535.

- 6. B. Tell, J. J. Weigand, J. Appl. Phys., 48 (1997) 5321
- 7. C. Kaito, A. Nonaka, S. Kimura, N. Suzuki, Y. Saito Y., J. Crystal Growth, 186, (1998) 386–392.
- 8. S. M. Pawar, B. S. Pawar, J. H. Kim, Oh-Shim Joo, C. D. Lokhande, Curr. Appl. Phys., 11-2 (2011) 117-161.

#### **GRANULATION OF POTASSIUM DIHYDROGEN PHOSPHATE**

K. Jančaitienė\*, R. Šlinkšienė

Department of Physical and Inorganic Chemistry, KTU Radvilėnų rd. 19, LT-50254 Kaunas, Lithuania \*Corresponding author, e-mail: <u>kristina.jancaitiene@ktu.lt</u>

The granulation of powders by size enlargement is desirable or necessary in many industrial processes. Segregation of powder constituents can be reduced by binding the powders together, in this way improving solid flow ability and reducing dust, which facilitate the product handling [1]. Approximately 60% of chemical industrial products are produced in granular form [2]. In the fertilizer industry, granulation is a key process. The handling of granules is more desirable than the

powder because less suspension particles are formed both inside the factory and/or during plantation. In addition, granulated fertilizers are more beneficial and functional than the powder products. Granulation can be carried out in different devices, differing by the amount of shearing imposed to the powder mass, such as: rotary drum, disk, fluidized bed, and spouted bed [3, 4].

In order to determine the optimal parameters of the granulation process (the composition of the raw material, the particle size, the moisture content) of various organic materials (microcrystalline cellulose of MC–1) suitable for production of high quality fertilizers, various mixtures of raw materials were granulated in laboratory conditions. Potassium dihydrogen phosphate was granulated by using 3 granulators of different types: rotary, a fluidized bed and a drum. Potassium phosphate granulation was investigated by changing the amount of water used for irrigation purposes as well as by adding a binder (cellulose). According to the obtained results, the fluidized bed and rotary granulators cannot be used to obtain granulated mono potassium phosphate as the granulometric composition does not meet the necessary fertilizer requirements. Granules (as a product) obtained from the rotary drum-type granulator were dried for approximately 16 hours in the heating oven at 60 °C. All the samples were cooled and fractioned, and then, the granulometric composition, the granule moisture and bulk were determined. The static strengths of granules of 1-2 and 2-3.15 mm fractions and the 10 % solution pH values were measured.

With 21.02 % moisture being present in the source materials, the obtained granulated product was denoted by the optimal granulometric composition as its commodity fraction constitutes 40.54 %.

The obtained results indicate that in order to obtain granulated potassium dihydrophosphate with optimal properties, the use of water does not suffice. It is also necessary to use other additives in order to improve the physical and mechanical properties of the pellets. Analysis of scholarly writings on the binding materials used in the granulation technology suggests that if the objective is to obtain maximally pure potassium dihydrophosphate, cellulose should be chosen as the binder as it contains no additional nutrients consumed by plants. In addition, cellulose is denoted by its cohesion properties.

- 1. Y.S. Cheong, M.J. Adams, M.J. Hounslow, A.D. Salman. Chem. Eng. Res. Des., 83 (2005) 1276–1278.
- 2. N. Balliu, I.T. Cameron. Powder Technol., 179 (2007) 12–24.
- 3. M. Olazar, M.J. San Jose, S. Alvarez, A. Morales, J. Bilbao. Ind. Eng. Chem. Res., 37 (1998) 4520–4527.
- 4. M. Olazar, M.J. San Jose, M.A. Izquierdo, S. Alvarez, J. Bilbao. Ind. Eng. Chem. Res., 40 (2001) 427–433.

## EVALUATION OF SOIL POLLUTION WITH HEAVY METALLIC ELEMENTS IN RAILWAY NEIGHBOURHOOD

## <u>Ā. Jansons</u><sup>1\*</sup>, A. Osīte<sup>1</sup>.

## <sup>1</sup> Faculty of Chemistry, University of Latvia, Jelgavas Street 1, LV-1004, Riga, Latvia \*Corresponding author, e-mail: <u>arisjanzons@gmail.com</u>

Railway is one of the main means of transportation, both for passengers and freight, due to its speed, precision and capacity, but proportionally to the number of passengers and freight transported, pollution of soil and air with inorganic and organic substances changes. Pollution of the environment with heavy metallic elements is quite common nowadays, but in most studies attention is focused on road transport as the main environmental pollutant with heavy metallic elements, forgetting about railway, which also makes a significant contribution to the pollution of the soil with heavy metallic elements [1].

Ion quantitative analysis of heavy metallic elements – iron, manganese, copper, zinc, nickel and lead has been carried out in soil samples, which were taken in Latvia from four railway station neighbourhoods with different railway transport movement intensity (A – Torņakalns, B – Jāņavārti, C – Kūdra, D – Dārziņi. Soil samples were taken within the braking distance and further from it, near the railway tracks and 10 meters from them. See *Fig. 1*. Firstly, preparation of collected soil samples for mineralization were carried out (drying, homogenization, sifting), then a destruction of soil sample matrix was performed by wet digestion with aqua regia, concentrated and diluted nitric acid in open system and at a microwave unit. The content of mentioned above heavy metallic elements in analysed soil samples were determined by use of flame atomic absorption spectrometry.

Several common trends were observed for all heavy metal element ions analysed. See *Fig.* 2. In all analysed soil samples which were collected within a breaking distance near the railway tracks there was significantly higher content of analysed heavy metal ions than in soil samples that were collected further from breaking distance 10 m from railway tracks.

It should be noted that there is no universal method for decomposition of different solid samples. The choice of the method of sample preparation depends on the object of study, composition of sample, availability of method and urgency of analysis [2]. Use of microwave unit for destruction of soil sample matrix with aqua regia and concentrated nitric acid provided the most complete extraction of analysed heavy metallic elements. Diluted nitric acid was successfully used to make a comparative evaluation of the prevalence of metallic element contamination in the soil, since diluted nitric acid cannot destroy soil minerals.



soil depending on soil collection place

1. N. Stojic, M. Pucarevic, G. Stojic, Transportation Research Part D, 2017, 57, 124-129.

2. V. I. Safarova, G. F. Shaidullina, T. N. Mikheeva, F. Kh. Kudasheva, N. R. Nizamutdinova, Innorganic Materials, **2011**, 47, 1512-1517.

## THE FORMATION OF CALCIUM HYDROXYAPATITE THIN FILMS ON STAINLESS STEEL SUBSTRATE

## V. Jonauske<sup>1,\*</sup>, Thomas C.K. Yang<sup>2</sup>, A. Kareiva<sup>1</sup>

<sup>1</sup>Department of Inorganic Chemistry, Institute of Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania <sup>2</sup>Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, 1, Sec. 3, Chung-Hsiao E. Road, Taipei, 106,Taiwan

<u>\*vilma.ciuvasovaite@gmail.com</u>

Calcium hydroxyapatite ( $Ca_{10}(PO_4)_6(OH)_2$ , CHAp) is the main inorganic component of natural human hard tissues. Synthetic CHAp is bioactive material, supports osteointegration of bone cells and does not show side effects from immune system [1-3]. Due to these properties CHAp is used in medicine for orthopedic devices, dental replacements, tissue engineering, antimicrobial coating applications [4, 5]. However, the mechanical weakness of the CHAp limits it's practical applications to those requiring little or no load bearing parts. For this reason, CHAp-coated metallic implants have the potential to be used for load-bearing implant applications in dentistry and orthopedics [6, 7]. Due to it's low cost, strong mechanical properties and good formability the most widely used material for medical and dental applications is 316L stainless steel [8, 9].

Sol-gel route for synthesis of thin films has some benefits over other methods such as simplicity, synthesis at low temperatures, effectiveness, suitability for complex-shaped implants and cost efficiency [10, 11].

In this work, the sol-gel synthesis of CHAp coatings on 316L stainless steel substrate was performed with further investigation of coatings behaviour in simulated body fluid (SBF). Calcium acetate monohydrate and phosphoric acid were used as precursors for the preparation of CHAp coatings. Spin-coating technique was employed to produce CHAp coatings. Approximately 0.2 ml of coating solution was placed on top of the 316L stainless steel substrate using syringe and then spin coated at 2000 RPM for 60 s in air. Substrates were annealed up to 15-30 times following the same procedure. Layers were heated in a furnace at 850 °C for 5 h. 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 anticorrosive effects of the sol-gel derived CHAp thin films on stainless steel substrate.

- 1. L.Q. Tri, D.H.C. Chua, Applied Surface Science, 256 (2009) 76-80.
- 2. I. Bogdanoviciene et al., Materials Research Bulletin, 41 (2006) 1754–1762.
- 3. D.-M. Liu et al., Biomaterials, 22 (2001) 1721-1730.
- 4. H.H. Beheri et al., Materials and Design, 44 (2013) 461-468.
- 5. M. Sygnatowicz, A. Tiwari, Materials Science and Engineering, 29 (2009) 1071-1076.
- 6. D.-M. Liu et al., Biomaterials, 23 (2002) 691–698.
- 7. B.-D. Hahn et al., Thin Solid Films, **519** (2011) 8085–8090.
- 8. T. Fu et al., Vacuum, 86 (2012) 1402-1407.
- 9. I. Gurappa, Surface and Coatings Technology, 161 (2002) 70–78.
- 10. H. Khandelwal et al., Applied Surface Science, 265 (2013) 30-35.
- 11. T. Kokubo et al., Biomaterials, 24 (2003) 2161–2175.

## ASSESSMENT OF HEAVY METALS CONTENT IN BEACH SEDIMENTS ALONG THE SOUTHEASTERN BALTIC SEA COAST (LITHUANIA)

## D. Karlonienė<sup>1,\*</sup>, D. Pupienis<sup>1,2</sup>, S. Tautkus<sup>1</sup>, A. Žarkov<sup>1</sup>

<sup>1</sup>Faculty of Chemistry and Geosciences, Naugarduko st. 24, Vilnius LT-03225, Lithuania <sup>2</sup>Nature Research Centre, Akademijos Str. 2, LT-08412 Vilnius, Lithuania \*Corresponding author, e-mail: dovile.karloniene@chgf.vu.lt

The large scale of anthropogenic activities (urbanization, industrialization and agriculture) has negative impact on the Baltic Sea because it is more susceptible to accumulate pollutants in surficial sediments due to the semienclosed system [1]. Heavy metals (HM) are among the most common environmental pollutants which can enter coastal environment by the air or rivers, accumulate and cause risks for human health and ecosystems. The aim of this study was to define the content of the main HMs (Cd, Cu, Cr, Ni, Pb and Zn) commonly considered technogenous origin in sandy beaches along the south-eastern Baltic Sea coast (Lithuania).

The beach along the south-eastern Baltic Sea coast is backed by a vegetated foredune or moraine cliffs. The beach consists predominantly of quartzose (enriched with heavy minerals) sand. The surface sand (0 - 5 cm) samples were collected along the Curonian spit and mainland sea coast of Lithuania (90 km) in the middle of the beach at equal distance of 5 km in 2014 [2, 3]. In total, 19 surface sand samples (3 replication, n=57) after mineralization in royal water (2 g digested in 10ml HCl:HNO<sub>3</sub> = 3:1) were analysed with the ICP AES.

The HM concentrations distributed following (average,  $mg \cdot kg^{-1}$ ): Zn(5.23) > Cr(1.28) > Pb(0.75) > Cu(0.56) > Ni(0.44) > Cd(0.08). The higher maximum and minimum HM concentrations were determined in the mainland coast than in the Curonian spit (Fig. 1.).



Fig. 1. The sum of the analysed HM concentrations distribution along the south-eastern Baltic Sea coast. The alongshore distance (0 km) is shown from Latvia border.//y axis – logarithmic scale.

The greatest mid-beach HMs values were defined in the sampling

site 25 km from the Latvian border with an active cliff area (average,  $mg \cdot kg^{-1}$ : Cd (0.24), Cr(1.70), Ni(1.043), Pb(1.38) and Zn (22.12)). Additionally, higher HMs values (average,  $mg \cdot kg^{-1}$ : Cd (0.37), Cu (1.97) and Cr (3.17)) were observed close to the border of Latvia where the beach is rich in peat and moraine deposits, which are exposed during the strong storms, and to the Šventoji resort where the beach might be affected by the anthropogenic activities (sewages from river, port).

- Belzunce Segarra, M.J., Szefer, P., Wilson, M.J., Bacon, J. & Bolałek, J., 2007. Baltic Sea. Pol. J. Environ. Stud. 16(4), 505-515.
- 2. Pupienis D., Buynevich I. V., Bitinas A. 2011. Journal of Coastal Research. SI 64, 1984–1988.
- 3. Pupienis D., Buynevich I.V., Jarmalavičius D., Žilinskas G., Fedorovič J. 2013. Journal of Coastal Research, SI. 65, 1844-1849

## PRESERVING WOOLLEN ARTWORK FROM ENVIRONMENTAL IMPACT -PROTEOMIC EXAMINATION OF WOOL'S KERATIN DEGRADATION DEPENDING ON ARTIFICIAL AGEING ATMOSPHERE

## M. Aksamit-Koperska<sup>a</sup>, J. C. Torres<sup>a</sup>, E. Bulska<sup>a</sup>

<sup>a</sup>Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Żwirki i Wigury 101,

#### Warsaw

e-mail: mkoperska@gmail.com

Preservation or heritage science is a cross-disciplinary scientific discipline that combines knowledge from science and art to preserve world cultural heritage. Decisions on the conservation of museum artefacts cannot be made without both thorough physicochemical analyses leading to the understanding of degradation mechanisms; and historic information on composition, handling and manufacturing process. A direct motivation of our study is the need to preserve (design storage atmosphere) XVI<sup>th</sup> century Jagiellonian tapestries (*Wawel arrases*) - a collection of tapestries commissioned by the Sigismund II Augustus to decorate the interiors of the Wawel Royal Castle in Cracow, Poland. Today this collection consists of 137 fabrics, from the original 365-piece group, which makes it the biggest, coherent tapestries set in Europe.

Poland has some of the worst air quality in Europe, with 33 of the continent's 50 most polluted cities, according to a World Health Organization (WHO) report from 2016. And in Cracow you can find one the of highest levels of suspended dust in Poland (composed of: elemental and organic Carbon, secondary organic and inorganic aerosols (including sulphate  $(SO_4^{2-})$ , nitrate  $(NO_3^{-})$  and ammonium  $(NH_4^+)$  ions) and trace elements including heavy metals). Fortunately, air let inside the museum is filtered and was proven free of major pollutants [1]. Nevertheless, the question of whether enclosing tapestries into frames with conditioned (e.g. oxygen-lean) atmosphere would be beneficial for the collection in the long-term remains unanswered.

Keratin from sheep's wool decomposes mainly by hydrolysis of peptide bonds and oxidation of individual amino acids and sulphur bonds; which can lead to liberation of peptides and formation of new functional groups in the protein chain with simultaneous release of volatile products. To understand the degradation process ongoing within the artwork we performed accelerated aging test of model sheep's wool textile samples. Temperature of 150 °C and 3 gaseous atmospheres (open reactor - air ventilated; closed reactor – air or nitrogen and volatile organic compounds VOCs mixture) were used as aging stimuli to simulate changes after long-term impact of oxygen, nitrogen and VOC's [3].

In previous work wool from tapestries and artificial ageing experiments have only been studied by spectroscopic techniques (ATR-FTIR, XRF or UV-Vis), which, due to the nature of the measurement, allowed to conclude only about surface processes of keratin degradation, specifically aminoacids oxidation (including sulphur bond oxidation). In this project we analyse sheep's *Ovies Aries* wool protein extract with nanoLC-ESI-QOrbitrap-MS spectrometric analyser to evaluate the state of overall oxidation and deamination of artificially aged keratin. Poster presents the results of the analysis of the proteins extract composition of artificially aged keratin from wool model samples and the resulting preliminary markers of thermal degradation of keratin.

#### *Thanks to: Wawel Royal Castle Museum and 2016/20/S/ST4/00149 National Science Centre grant.* Bibliography:

[1] Norsk Institutt for Luftforskning measurements during grant 11/03/2009/FWK Development of a conservation cassette for the safe display of silk banners

[3] M.A. Koperska, D. Pawcenis, J. Bagniuk, T. Łojewski, J. Łojewska, Degradation markers of fibroin in silk through infrared spectroscopy, Polymer Degradation and Stability 105 (2014),185–196.

## APPLICATION OF *PLEUROTUS OSTREATUS* IN DEGRADATION OF SELECTED ANTIDEPRESSANTS

## <u>B. Kózka</u><sup>1\*</sup>, J. A. Drobniewska<sup>1</sup>, M. Klimaszewska<sup>1</sup>, J. Turło<sup>1</sup>, G. Nałęcz-Jawecki<sup>1</sup>, Giebultowicz<sup>1</sup>

<sup>1</sup>Medical University of Warsaw – Faculty of Pharmacy, Banacha 1, 02-097 Warsaw, Poland \*Corresponding author, e-mail: <u>jgiebultowicz@wum.edu.pl</u>

The presence of pharmaceuticals in effluents from the <u>sewage treatment plants</u> is a huge problem discussed worldwide [1]. Since the effluents are introduced to the surface water, the pharmaceuticals can exert an toxic effect both to the aquatic environment and to human [2]. In order to minimize the risk of the toxic effects, novel methods of the sewage treatment should be introduced. One of the method could be application in the biological treatment of wastewater the organism, that could degrade these compounds, like fungus from *Basidiomycota* [3].

The aim of this study was to determine the ability of fungus from *Basidomycota* named as *Pleurotus ostreatus* to degrade selected active pharmaceutical ingredients (n=8). Moreover, the activity of ligninolytic enzymes was assessed.

The *P. ostreatus* cultures were carried out for five days in Sabouraud Dextrose Broth medium. Active pharmaceutical ingredients were quantified by validated LC-MS method. The activity of the enzymes was assessed spectrophotometrically using standard methods.

The obtained results show, that the totally-degraded active pharmaceutical ingredients are clomipramine and mianserin. Somewhat less, but still on high level, are degraded paroxetine, fluoxetine and sertraline. Degradation degree below 50% value occurs in the case of escitalopram and venlafaxine. Activity of laccase and lignin peroxidase belonging to ligninolytic enzymes was three times higher in the presence of the examined compound in cultivation medium.

To conclude, *P. ostreatus* can be useful in degradation of pharmaceuticals. However, to confirm the utility of the fungus to wastewater treatment more research are needed.

- 1. D.Ashton, M.Hilton, K.V.Thomas, Science of The Total Environment 333 (2004) 167-184
- 2. L.J.G. Silva, C.M Lino, L.M. Meisel, A. Pena, Science of the Total Environment 437 (2012) 185–195
- 3. M. Alcalde, M. Ferrer, F.J. Plou, A. Ballesteros, Trends in Biotechnology 24 (2006) 281-287)

## STABILITY OF PES/PVC ARCHITECTURAL TEXTILE UNDER ENVIROMENTAL EXPLOTATION

## V. Sacevičienė<sup>1</sup>, N. Dukštienė<sup>2</sup>, <u>V. Krylova<sup>2,\*</sup></u> S. Žalenkienė<sup>2</sup>,

<sup>1</sup>Institute of Architecture and Construction, Tunelio St. 60, 44405 Kaunas, Lithuania <sup>2</sup>Kaunas University of Technology, Radvilenu St. 19, 50254 Kaunas, Lithuania \*Corresponding author, e-mail: valentina.krylova@ktu.lt

PES (polyester) coated PVC (polyvinylchloride) fabric (PES/PVC) is one of the most commonly applied architectural textiles in many modern architecture projects because of its excellent synergy of functionality and aesthetics [1-2]. Growing demand to apply this textile material instead of traditional building materials encourage to investigate factors reducing withstand initial properties of (PES/PVC) over time. The majority of works confirm the degradation of PES/PVC mechanical properties under exposure to outdoors weathering or high-low temperature conditions [3].

The aim of this work is to determine the chemical compositional changes of these architectural materials exposed to different artificially aging conditions. The commercially available PES/PVC architectural textile produced by VERSEIDAG Coating & Composite (Germany) investigated. Aging experiments carried out following the general requirements and analysis methodologies described in ISO 9142:2003. To verify the chemical composition changes, the wavelength dispersive X-ray spectroscopy (RRF) and Energy dispersive X-ray spectroscopy in conjunction with scanning electron microscopy (EDX/SEM) applied.



Fig. The EDX spectrum of the PES/PVC architectural textiles: (a) initial; (b) after UV radiation

XRF and EDX results analysis show that under ultraviolet radiation and temperatures higher than 30 °C polyvinylchloride colourless and split off hydrogen chloride:

 $[CH_2=CHCl]_n \rightarrow [CH_2=C=]_n + HCl.$ 

The comparison of SEM images obtained from non-aged and aged PES/PVC samples shows significant changes in fabric's structure. The aging destroys architectural textile and partially opens polyester fabrics fibres.

- 1. C. Paech, Procedia Eng., 155 (2016) 61-70.
- 2. K. Göppert, C. Paech, Steel Construction, 4 (2015) 237-243.
- 3. D.K. Hwang, Y.G. Shul, Y.H. Chu, Polym. Compos., 36 (2015)1462–1468.

## DETERMINATION OF TRIBUTYLTIN IN SEDIMENTS OF SZCZECIN LAGOON

D. Kucharski<sup>1</sup>\*, P. Drzewicz<sup>2</sup>, K. Mianowicz<sup>3</sup>, A. Skowronek<sup>2</sup>, G. Nałęcz-Jawecki<sup>1</sup>, J. Giebultowicz<sup>1</sup>

1) Medical University of Warsaw, Zwirki i Wigury 61, 02-091 Warsaw, Poland

2) Polish Geological Institute - National Research Institute, Rakowiecka 4, 00-975 Warszawa, Poland
 3) University of Szczecin, Jana Pawla II 22a, 70-453 Szczecin, Poland
 \*Corresponding author, e-mail: dkucharski@wum.edu.pl

The Szczecin's Lagoon is a shallow coastal lagoon of high economic and ecological value. There are two large seaports in Swinoujscie and Szczecin. InSzczecin is located also shipyard industry. On the other side, that region is inhabited by numerous species of fish, birds and aquatic organisms, which are protected by European Union Program Natura 2000. The level of the contamination of the lagoon depends on many factors. One of the most important micropollutants, mainly due to persistence, are compounds accumulated in the sediments. Among them the tributyltin (TBT) is characterized by high accumulation potential. TBT was widely used as a component of paints, that prevents ships from fouling by the aquatic organisms [1]. However, due to high toxicity of TBT, it was banned by the European Union in 2003[2]. At present, the monitoring of TBT level in Szczecin's Lagoon area is not carried out and no scientific publications are available. It is important to determine which areas of lagoon are mostly contaminated by TBT. These data will allow for taking appropriate decisions related to the protection of the natural environment of this area.

The main goal of our research was to determine the concentration of TBT in samples from different parts of Szczecin's Lagoon. We examined 64 probes of lyophilized and sifted sediments. The samples extraction was carried out using the validated Quechers method. The quantitative analysis was performed on high performance liquid chromatograph coupled to mass spectrometer (LC-MS). Only in four samples the TBT concentration was below the limit of quantitation (1 ng/g). In other samples it ranged from 14.4 to 4300 ng/g of the sediment. The average concentration was 300 ng/g. Our results show that the level of TBT in Szczecin's Lagoon is higher than in open sea areas and is characteristic of the areas near big seaports [3]. **References** 

- 1. Hoch M., Appl. Geochem. 16 (2001) 719-743.
- 2. Regulation EC, No 782, (2003).
- 3. Antizar-Ladislao B., Environ. Int., 34 (2008), 292–308.

The project was financed by National Science Center in Poland OPUS 11 (UMO-2016/21/B/ST10/02391)

#### **CO2 SORPTION BY HETEROGENEOUS SORBENTS BASED ON ACTIVATED CARBON**

#### A. Ruchajus, G. Dabrilaitė-Kudžmienė, A. Jaskūnas, S. Kitrys

Kaunas University of Technology, Radvilenu st.19, LT-50254 Kaunas, Lithuania Corresponding author, e-mail: gitana.dabrilaite@ktu.lt

In recent years research and development of multi-component heterogeneous systems for different applications is very interesting for scientists because they can possess very broad spectrum of properties. One of those systems are adsorbents and liquid chemosorbents that can be used for abatement or concentration of components. Such heterogeneous systems are useful even in industrial production because it is usually followed by accumulation of by-products. Such by-products usually are harmful for production itself or might make negative impact on the environment. In general, sorbtive methods for abatement or purification are the most effective and energy efficient removal techniques, so research and development of new, cheap and effective sorbents that possess high adsorptive/absorptive capacity are of great importance.

One of the most important components, that should be removed from gas streams and concentrated, is carbon dioxide. It is interesting both from large-scale production and from environmental point of view. Usually pressure swing adsorption (PSA) or absorption by amino alcohols are employed for CO<sub>2</sub> removal and partial purification [1, 2]. Nevertheless, the main downsides associated with aforementioned techniques are high amount of energy needed for recovery of used sorbents, high prices of amino alcohols, inconvenient storage and transportation of liquid amino alcohol sorbents. The main aim of this work was to research and develop heterogeneous sorbent based on activated carbon that has thermal stability and high surface area impregnated with amino alcohols and potassium carbonate that have high affinity for CO<sub>2</sub>. Activated carbon (AC) WS-42 was used for studies that was impregnated with pure methyldiethanolamine (MDEA), monoethanolamine (MEA) as well as K<sub>2</sub>CO<sub>3</sub> aqueous solutions. During the experiments concentration of CO<sub>2</sub> was kept constant at 40 % which similar to concentration of CO<sub>2</sub> in the biogas. As results showed, activated carbon impregnated with MEA and K<sub>2</sub>CO<sub>3</sub> were the best sorbents because they had the highest sorbtive capacity (in one-hour duration) for CO<sub>2</sub> – 22-24 mg/g and 27-29 mg/g respectively. Meanwhile MDEA/AC sorbent took up 10-11 mg/g of carbon dioxide at the same conditions. Nevertheless, MDEA/AC sorbent had the highest static strength of granules.



Fig. Sorption kinetics of 40 % CO2 at 25 °C on: 1 – K2CO3/AC; 2 – MEA/AC; 3 – MDEA/AC

- 1. I. M. Bernhardsen, H. K. Knuutila, Int. J. Greenh. Gas Con., 61 (2017) 27-48.
- 2. S. Lee, S. Park, J. Ind. Eng. Chem., 23 (2015) 1-11.

## DETECTION OF C4 PLANT SUGAR IN ADULTERED HONEY USING IRMS AND UHPLC CHROMATOGRAPHY

## K. D. Labsvārds<sup>1\*</sup>, L. Buša<sup>1</sup>, K. Meile<sup>2</sup>, A. Vīksna<sup>1</sup>

<sup>1</sup>University of Latvia, Faculty of Chemistry, Jelgavas 1, LV-1004 Riga, Latvia <sup>2</sup>Latvian State Institute of Wood Chemistry, Dzerbenes 27, LV-1006, Riga, Latvia \*Corresponding author, e-mail: <u>kriss.labsvards@gmail.com</u>

Honey is a sweet, viscous food substance produced by bees from floral nectar. Natural bee honey is a unique sweetening agent that can be used by humans without processing. However, honey can easily be adulterated with various cheaper sweeteners, resulting in higher commercial profits [1]. Commonly used adulterants include high fructose corn syrup, maltose syrup, refined beet and cane sugar etc. Stable isotope ratio mass spectrometry (SIRMS) can be used to determine the adulteration of honey with C4 plant (corn or cane) sugar since its  $\delta^{13}$ C values are around -10‰ to -20‰ but bees use floral nectar from C3 plants which  $\delta^{13}$ C values are about -22‰ to -33‰. Significant  $\delta^{13}$ C value difference between honey and its protein provide valuable information of honey authenticity [2,3].

Five adulterated honey samples were made adding different amounts of sugarcane sucrose syrup (3%, 6%, 9%, 12%, 15%) to pure honey. The protein from the honey was extracted using dialysis membrane with MWCO 12 kDa. Determination of  $\delta^{13}$ C ratios in protein and honey was carried out with Nu Horizon SIRMS at the University of Latvia, using certified organic reference materials USGS-40 and USGS-41 (L-Glutamic acid). The  $\delta^{13}$ C values are expressed relative to VPDB. Waters Acquity UHPLC system with Waters Acquity UHPLC BEH Amide column (100 mm × 2.1 mm,  $\emptyset$  1.7 µm) combined with Waters ELSD detector were used to determine weight fraction of sucrose in pure and adulterated honeys.





Despite dissimilar results of calculated and detected amount of sucrose compared to actually added amount (Figure 1), results show expected increase in  $\delta^{13}$ C values as C4 plant adulterant concentration increases. Only adulterated honeys with added sucrose content higher than 6% have high enough  $\delta^{13}$ C value difference between honey and protein to calculate amount of added sucrose. UHPLC method did not provide exact quantitative information of components which concentrations are lower than 5%.

- 1. M. Oroian, Ropciuc S., Paduret S., Food Anal. Methods, 138 (2017) 148-156.
- 2. Chua L.S., Lee J.Y., Chan G.F., Anal. Bioanal. Chem., 405 (2013) 3063-3074.
- 3. Wu L., Du B., Heyden Y. V., Chen L., Zhao L., Wang M., Xue X., Trends in Anal. Chem., 86 (2017) 25-38.

## ON THE SOLVOTHERMAL SYNTHESIS OF Me2(H2O)4(5SSA)3·DMF AND Me2(H2O)4(4NSA)2·DMF COORDINATION POLYMERS

## Andrius Laurikenas<sup>1</sup>, Fatma Yalçin<sup>2</sup>

<sup>1</sup>Department of Inorganic Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania <sup>2</sup>Department of Chemistry, Institute of Natural Sciences, Bolu Abant Izzet Baysal University, Gölköy Yerleşkesi, 14030, Bolu, Turkey

Reactions of  $Me^{x+}NO_3*yH_2O$  ( $Me^{x+} = Fe^{3+}$ ,  $Ni^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ) with respectively 4-nitrosalycilic (4NSA) and 5sulfosalicylic (5SSA) acids using solvothermal synthesis [1] method produced coordination polymers composed of  $Me^{x+}$  atoms and organic fragments which include three different functional groups, carboxylic, hydroxyl, and sulfonic [2], each coordinated to the  $Me^{x+}$  atoms. The phase and chemical composition, microstructure and properties of  $Me_2(H_2O)_4(5SSA)_3$ •DMF and  $Me_2(H_2O)_4(4NSA)_2$ •DMF coordination polymers were evaluated and discussed. Synthesized coordination polymers were characterized by X-ray diffraction (XRD) analysis, infrared (FTIR) spectroscopy, scanning electron microscopy (SEM).

#### References

[1] J.F. Ma, J. Y. Shun, S.Y. Song. Two Coordination Polymers of Ag(I) with 5-Sulfosalicylic Acid, Cryst. Growth Des. 5, 807-812 (2005).

[2] *M. Hemamalinia*, *H.-K. Funa*. 2-Amino-4-methyl-pyridinium 3-carboxy-4-hydroxybenzenesulfonate monohydrate, *Act. Cryst.* **66**, 2095–2096 (2006).

## P 34

# THE VARIATION OF PHOSPHORUS, SULFUR AND NITROGEN IN LICHENS DEPENDING ON LOCALIZATION AREA

## V. Lazarenko\*, Z. Balcerbule, V. Rudoviča

Faculty of Chemistry, University of Latvia, Jelgavas street 1, LV-1004, Riga, Latvia \*e-mail: <u>bonza1@inbox.lv</u>

Lichens (*lichenes*) belong to the group of symbiotic organisms which consist of two components: fungi and algae. Lichens absorb water and nutrients directly from the air and therefore, they are sensitive to the air pollution, especially SO<sub>2</sub> is considered as the most hazardous substance which may negatively affect the population of lichen species.

The aim of our research was to analyze the content of phosphorus, sulfur and nitrogen in lichens and in respective soil.

Lichens samples (on the ground and on trees) were collected in 3 different locations in Balvi and Viļaka districts, with a distance of 10-30 km between them:

- the area of the former Kuprava drain pipe factory (Kuprava parish);
- the area of the former landfill (Kubuli parish);
- the Sita forest (Kubuli parish).

When choosing sampling sites of lichens, it was important to verify the influence of the former Kuprava drain pipe factory, which operated during the period from 1971-1992 and used the Kuprava deposits for the production of drain pipes, ceramic pebbles and bricks. These times surrounding area was covered with clay dust, simultaneously mazut was intensively used as fuel.

The dry mineralization of samples was performed to determine the content of phosphorus and sulfur by applying spectrophotometric method. In turn, the Kjeldahl method was chosen to determinate the total content of nitrogen. The research results show that on the lichens collected from the leafy trees (*Xanthoria parietina*) phosphorus content is ~1.3 g/kg irrespective of their growing site (the former drain pipe factory, forest, or landfill). At the distance of 25 km from the factory, phosphorus content on the ground grown scrub lichens (*Cladina rangiferina*) decreases approximately twice (from 0.9 g/kg to 0.5 g/kg). Sulfur content in lichens (*Cladina rangiferina*) in the Balvi and Viļaka districts is almost the same ~0.3 g/kg.

When determining the amount of phosphorous in lichens collected at the former drain pipe factory (*Peltigera collina*), the increment of the phosphorus content was observed depending on the lichens growth site according to the following order: land  $\rightarrow$  tree  $\rightarrow$  stone or 0.9 g/kg  $\rightarrow$  4.0 g/kg  $\rightarrow$  7.7 g/kg.

The analysis of soil samples shows a correlation between the content of phosphorus, sulfur and nitrogen in the soil and in the lichens from the same areas - as the concentration of these elements in the soil increases, similar changes are observed in the concentration of these elements in the lichens.

## CHALLENGES OF DETERMINING LEVOGLUCOSENONE BY UHPLC IN PYROLYSIS PRODUCTS

## K. Meile<sup>1,2\*</sup>, D. Godina<sup>1,2</sup>, A. Zhurinsh<sup>1</sup>, R. Pomilovskis<sup>1</sup>

<sup>1</sup>Latvian State Institute of Wood Chemistry, Dzerbenes 27, LV-1006 Riga, Latvia <sup>2</sup>University of Latvia, Jelgavas 1, LV-1004 Riga, Latvia \*kristine.meile@inbox.lv

Levoglucosenone (LGO) is a lignocellulose derived chemical with a high potential in the chemical synthesis industry. Because of its two chiral centers LGO is suitable for the synthesis of stereospecific compounds in pharmacy and "green" solvents [1]. LGO is obtained from biomass, such as wood, by cellulose dehydration and thermal decomposition [2]. In this study LGO was obtained by catalytic pyrolysis of birch (*Betula pendula*) wood impregnated with phosphoric acid.

In the pyrolysis process LGO is recovered in the condensable fraction of pyrolysis products along with numerous other chemical compounds – cellulose derived anhydrosaccharides, furans and organic acids, and lignin derived phenols. This mixture is most often analyzed by gas chromatography with flame ionization detection or mass spectrometry. High performance liquid chromatography can also be used, but there are often problems with the separation of LGO and 5-hydroxymethylfurfural [3]. Since ultra-high performance liquid chromatography (UHPLC) is becoming more and more widespread in analytical laboratories, the aim of the presented study is to evaluate the possibilities of LGO determination in pyrolysis products with UHPLC-UV-MS.

The method development consisted of choosing a suitable UHPLC column, optimizing the mobile phase composition, selecting the best UV detection wave length and developing a quadrupole MS detection method for quantitative analysis. Eventually, a WATERS UPLC CSH Phenyl-Hexyl column ( $100 \times 2.1 \text{ mm}$ ,  $1.7 \mu\text{m}$ ) with 0.1 % formic acid in water/acetonitrile gradient was used, which allowed sufficient separation of LGO and 5-hydroxymethylfurfural ( $\alpha = 1.5$ ), as well as other by-products – levulinic acid, furfural and phenols. UV detection at 220 nm and 350 nm was compared, as well as MS single ion recording at 97 and 127 Da. Acceptable precision, reproducibility, linearity and sensitivity was achieved, however, concerns arise because of the involuntary degradation of LGO in aqueous solutions, which can lead to a decreased result.

This research was supported by the ERDF project No. 1.1.1/16/A/010 "Developing an innovative technology for producing levoglucosenone from lignocellulose".

## SOL – GEL SYNTHESIS OF ELECTROCHEMICALLY ACTIVE MOLYBDENUM OXIDE COATINGS

## <u>A. Minderytė<sup>1</sup></u>, S. Butkutė<sup>2,\*</sup>, M. Skruodienė<sup>1,2</sup>, M. Petrulevičienė<sup>2</sup>, I. Savickaja<sup>2</sup>, B. Šebeka<sup>2</sup>, A. Selskis<sup>2</sup>, J. Juodkazytė<sup>2</sup>, R. Ramanauskas<sup>2</sup>

<sup>1</sup>Institute of Chemistry, Vilnius University, Naugarduko st. 24, LT-03225 Vilnius, Lithuania <sup>2</sup> Center for Physical Sciences and Technology, Saulėtekio av. 3, LT-10257 Vilnius, Lithuania \*Corresponding author, e-mail: skirmante.butkute@ftmc.lt

Lately the demand for cheap and adequate seawater desalination systems is growing as water for drinking, agriculture and industry is critical to human habitation on this planet. Electrochemical water desalination is one of the most promising technologies [1]. As molybdenum oxides show great properties of intercalation of small ions (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, and H<sup>+</sup>) they can be used in capacitive deionization systems [2]. Thus the aim of this study is to synthesize electrochemically active coatings of molybdenum oxide with large surface area.

The molybdenum oxide coatings were prepared by sol – gel dip-coating method. The influence of used solvent on the coating quality was examined. Besides, variety of synthesis parameters such as gel pH, concentration of the molybdenum precursor, annealing temperature and number of layers were investigated. Obtained films were thoroughly analyzed employing techniques listed further: quality and layer dispersion on substrate - optical microscope, coating morphology – scanning electron microscopy (SEM), elemental compositions – X-ray energy-dispersive spectroscopy (EDS) and phase composition – X-ray diffraction (XRD) analysis. The suitability of obtained coatings to be used as electrodes for water electrolysis and desalination was investigated using cyclic voltammetry.

It was found that the annealing temperature determines which of two most common MoO<sub>3</sub> phases, orthorhombic  $\alpha$ -phase or metastable monoclinic  $\beta$ -phase, is dominant in the final product [3]. As 350 °C temperature is critical for phase transition of MoO<sub>3</sub>, the obtained coatings contained both phases. XRD results showed that  $\beta$  – MoO<sub>3</sub> phase is dominant in the samples annealed at 300 °C and  $\alpha$  – MoO<sub>3</sub> phase prevails in the samples heated at 350 °C. The homogenous coating with rod-like morphology (Fig. 1) was formed from gel containing 2-methoxyethanol after annealing at 300 °C.



Fig. 1. SEM picture of  $MOO_3$  coating annealed at 300 °C.

- 1. Alkaisi, R. Mossad, A. Sharifian-Barforoush, Energy Procedia, 110 (2017) 268-274.
- 2. S.-Y. Lin, C.-M. Wang, K.-S. Kao, Y.-C. Chen, C.-C. Liu, J Sol-Gel Sci Techn, 53 (2010) 51-58.
- 3. I.A. de Castro, R.S. Datta, J.Z. Ou, A. Castellanos-Gomez, S. Sriram, T. Daeneke, K. Kalantar-zadeh, Adv. Mater., 29 (2017) 1701619.

## ON THE CALCIUM SUBSTITUTION EFFECTS IN Sr(4-x)Ca(x)Al14O25 DOPED WITH CERIUM

<u>M. Misevicius</u><sup>1,2,\*</sup>, V. Balevicius<sup>1</sup>

<sup>1</sup>Institute of Chemical Physics, Faculty of Physics, Vilnius University, Saulėtekio al. 3, LT-10257 Vilnius, Lithuania

<sup>2</sup>Institute of Chemistry, Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko street 24, LT-03225 Vilnius, Lithuania

\*Corresponding author, e-mail: martynas.misevicius@chf.vu.lt

Materials with advanced optical properties is one of the main focuses of current chemistry research and development. Such materials have a wide variety of applications in screen or laser production, Light Emitting Diode (LED) technology and medicine. One of the system, that interests scientists in the field of luminescence, is SrO–Al<sub>2</sub>O<sub>3</sub> which has a number of different phases that have been described in literature [1]. One of the most promising systems is Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub> phase which doped with Eu<sup>2+</sup> and Dy<sup>3+</sup> has blue-green emission. Moreover, these materials also have the property of persistent luminescence and can exhibit afterglow time up to 15 hours [2]. In recent years there has been a lot of research done in the field of persistent luminescence, and one of the applications of such materials could be to improve the development of new generation LED, which could help us greatly reduce our energy consumption. But the main applications of phosphors at the moment are in safety indications, emergency lighting and graphical arts.

The current study aims on expanding the knowledge related to strontium aluminates in perspective of persistent phosphors. The goal of this research was to improve luminescent properties of cerium-doped  $Sr_4Al_{14}O_{25}$ . In this study,  $Ce^{3+}$  was chosen as an activator as it is one of most promising ions in non-Eu<sup>2+</sup> based persistent phosphors [3]. Cerium is cheaper and requires milder reducing conditions in comparison to europium, so efficient  $Ce^{3+}$  based persistent phosphor might lead to commercially competitive product in the market.

During this work, a series of cerium-doped Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub> samples with partial substitution of Sr by Ca were prepared by solid-state synthesis method. Prepared materials were characterized using powder X-ray diffraction and obtained data was analyzed employing Rietveld refinement method to determine crystal structure properties, such as unit cell parameters and site occupancies. Luminescence measurements were carried out to record excitation and emission spectra, luminescence decay times and quantum efficiencies.

## Acknowledgement

The study was funded from the European Community's social foundation under Grant Agreement No. 09.3.3-LMT-K-712-02-0114.

- 1. A. Douy, M. Capron, J. Eur. Ceram. Soc., 23 (2003) 2075-2081.
- 2. Y. Lin, Z. Tang, Z. Zhang, Mater. Lett., 51 (2001) 14-18.
- 3. K. Van den Eeckhout, D. Poelman, P. Smet, Mater., 6 (2013) 2789-2818.
### LUMINESCENCE CHARACTERIZATION OF AIN NANOTUBE/CsI SCINTILLATOR AND AIN NANOTUBE/POLYMER COMPOSITES FOR MEDICAL APPLICATION

# <u>A. Moskina</u><sup>1</sup>, A.I. Popov<sup>1</sup>, V. Savchyn<sup>2</sup>, C. Balasubramanian<sup>3</sup>, O.I. Aksimentyeva<sup>4</sup>, E. Elsts<sup>1</sup>, L. Myasnikova<sup>5</sup>, A. Barmina<sup>5</sup>, N. Zhanturina<sup>5</sup>, S. Sagimbaeva<sup>5</sup>, D. Sergeyev<sup>5</sup>, K. Shunkeyev<sup>5</sup>

<sup>1</sup>Institute of Solid State Physics, University of Latvia, Latvia <sup>2</sup>Ivan Franko National University of Lviv, 79017 Lviv, Ukraine <sup>3</sup>Institute for Plasma Research, Bhat, Gandhinagar, 382 044. India <sup>4</sup>Zhubanov Aktobe Regional State University, Aktobe, Kazakhstan e-mail: popov@latnet.lv

Nanostructures of Aluminium Nitride (AlN) – nanotubes, nanowires and nanoparticles have been successfully synthesised by using a high temperature, highly non-equilibrium DC arc plasma method and investigated with different spectroscopy methods, including XANES, FTIR, neutron powder diffraction and inelastic neutron scattering [1-3].

Here we report the results of the cathodoluminescence studies of the AlN nanotubes and nanoparticles, which have been measured between 80 K and room temperature (RT) under electron irradition with 10 keV energy. Low-temperature CL spectra of nanostructured AlN have been compared with those of the commercially available AlN powder. The significant difference between emission spectra of the three investigated samples has been established. Commercial AlN has been found to emit a band peaked at 3.47 eV which is commonly ascribed to oxygen impurities. Emission of the AlN nanoparticles is centered around 3.66 eV while CL spectrum of AlN nanotubes show complex character with at least three peaks at 2.2, 3.0 and 3.5 eV in the photon energy range of 1.8 - 3.8 eV. CL intensity of the nanostructured samples has been found to decrease significantly at RT, most probably due to a combination of non-irradiative relaxations at the surface, electron-phonon interactions and the reabsorption of the emitted light. CL of AlN-nanotube/CsI-scintillator composites has been also studied. Energy transfer via luminescence emission from CsI scintillator to AlN nanotube is demonstrated. Luminescence properties AlN nanotube/polymer composites were also studied and compared with those obtained for AlN nanotubes and nanoparticles.

- 1. Balasubramanian C., et al. Journal of Physics: Condensed Matter 18 (2006): S2095.
- 2. Bellucci S., Popov A.I. et al. Radiation Measurements 42 (2007): 708-711.
- 3. Bellucci S., Balasubramanian C., Ivanov A., Popov A., Schober H. J. Neutron Research, 14(2006); 287-291.

# ON THE SYNTHESIS AND CHARACTERIZATION OF BISMUTH FERRITE – BARIUM TITANATE SOLID SOLUTIONS

# <u>A. Pakalniškis<sup>1</sup></u>, L. Fadlyani<sup>2</sup>, I. Grigoraviciute-Puroniene<sup>1</sup>, A. Morkan<sup>2</sup>, Z. Stankeviciute<sup>1</sup>, A. Žarkov<sup>1</sup>, I. Morkan<sup>2</sup>, R. Skaudžius<sup>1</sup>, A. Kareiva<sup>1</sup>

<sup>1</sup>Institute of Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania

<sup>2</sup>Department of Chemistry, Faculty of Arts and Sciences, Abant Izzet Baysal University, Bolu 14280, Turkey

Over the last few years BiFeO<sub>3</sub> has attracted much attention as a multiferroic material with both ferroelectric and ferromagnetic properties. However it is nearly impossible to obtain pure BiFeO3 without secondary phases of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>, Bi<sub>25</sub>FeO<sub>40</sub>, or Bi<sub>46</sub>Fe<sub>2</sub>O<sub>72</sub> [1]. But recently it was shown that by synthesizing BiFeO<sub>3</sub> as solid solutions with other perovskite structure materials, the main phase can be stabilized and the appearance of secondary phases can be avoided [2, 3]. One of such systems is the BiFeO<sub>3</sub>–BaTiO<sub>3</sub> solid solution [4]. Such composites show high Curie temperature and can be potentially applied in high temperature piezoelectric applications [5].

In this study, the 1-xBiFeO<sub>3</sub>–xBaTiO<sub>3</sub> (x = 0.1-0.9) and strontium doped 0.7BiFeO<sub>3</sub>–0.3Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> (x = 0-1) composites were prepared by citric acid and ethylene glycol assisted sol-gel method. In all cases precursors were ground in an agate mortar and heated at 650 °C for 5 h. For the characterization of obtained samples X-ray diffraction (XRD) analysis was used to determine the purity of samples. Dynamic light scattering (DLS) was used to obtain the relative size of the particles and scanning electron microscopy (SEM) was used to determine the shape of the particles. The results of this study showed that the selected sol-gel method was suitable for the fabrication of 1-xBiFeO<sub>3</sub>–xBaTiO<sub>3</sub> and 0.7BiFeO<sub>3</sub>–0.3Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> (x = 0-1) composites.

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 Sklodowska-Curie grant agreement No. 778070.

 F.P. Gheorghiu, A. Ianculescu, P. Postolache, N. Lupu, M. Dobromir, D. Luca, L. Mitoseriu Journal of Alloys and Compounds, 506 (2010), pp. 862-867.
 M.T. Buscaglia, L. Mitoseriu, V. Buscaglia, I. Pallecchi, M. Viviani, P. Nanni, A.S. Siri Journal of the European Ceramic Society, 26 (2006), pp. 3027-3030.
 M.M. Kumar, A. Srinivas, S.V. Suryanarayana Journal of Applied Physics, 87 (2000), pp. 855-862.
 J. Rödel, W. Jo, K.T.P. Seifert, E.M. Anton, T. Granzow, D. Damjanovic Journal of the American Ceramic Society, 92 (2009), pp. 1153-1177.
 S.O. Leontsev, R.E. Eitel Journal of the American Ceramic Society, 92 (2009), pp. 2957-2961.

# INVESTIGATION ON AFFECT OF HYDROTERMAL SYNTHESIS CONDITIONS FOR EUROPIUM DOPED GADOLINIUM PHOSPHATE NANOPARTICLES SIZE AND MORPHOLOGY

A. Pakalniškis<sup>1</sup>, R. Skaudžius<sup>1</sup>

<sup>1</sup>Institute of Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania

e-mail: andrius.pakalniskis@chgf.stud.vu.lt

Over the last couple of decades interest in biocompatible nanomaterials has been increasing. One such material is  $GdPO_4$  because of the phosphate groups on its surface and its stability [1]. Due to the presence of strongly paramagnetic  $Gd^{3+}$  that have seven unpaired 4f electrons, this material is a suitable candidate as a contrast material for paramagnetic resonance imaging. Moreover  $GdPO_4$  is an excellent matrix for doping with rare earth elements in order to obtain a multifunctional magnetic and luminescent material. Europium attracted biggest amount of attention among rare earth elements due to long decay time, narrow emission bands and orange-red emission light [2]. However biological application require smaller than 100 nm particles size. It is also reported that GdPO<sub>4</sub> has multiple possible crystallographic structures [3, 4]. All these factors as well as morphology influence the luminescent and magnetic properties of materials so it is important to obtain monodisperse nanoparticles, what is difficult to achieve even now and special methods are used [5].

In this work, europium doped gadolinium phosphate was prepared using citric acid assisted hydrothermal synthesis. Conditions like temperature, pH, heating time, pressure or concentration were changed in order to determine the effect on the final product in an attempt to obtain monodisperse single phase powders. For the characterization of powders X-ray diffraction (XRD) analysis was used to determine the purity of samples, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) was used to determine the shape and size of the particles. Luminescence was also measured.

Acknowledgements. This work was financed by "Lietuvos mokslo taryba" in the frame of the project " Studentų gebėjimų ugdymas dalyvaujant mokslinėse vasaros praktikose". Nr. 09.3.3-LMT-712-09

- 1. Dumont, M.F., et al., DNA Surface Modified Gadolinium Phosphate Nanoparticles as MRI Contrast Agents. Bioconjugate Chemistry, 2012. 23(5): p. 951-957.
- 2. Patra, C.R., et al., Inorganic phosphate nanorods are a novel fluorescent label in cell biology. J Nanobiotechnology, 2006. 4: p. 11.
- 3. Fang, Y.-P., et al., Systematic Synthesis and Characterization of Single-Crystal Lanthanide Orthophosphate Nanowires. Journal of the American Chemical Society, 2003. 125(51): p. 16025-16034.
- 4. Rodriguez-Liviano, S., et al., Synthesis and Properties of Multifunctional Tetragonal Eu: GdPO4 Nanocubes for Optical and Magnetic Resonance Imaging Applications. Inorganic Chemistry, 2013. 52(2): p. 647-654.
- 5. Whitesides, G.M., The "right" size in nanobiotechnology. Nature Biotechnology, 2003. 21: p. 1161.

### PREPARATION OF HUMIC SUBSTANCES AND THEIR APPLICATION FOR THE PRODUCTION OF FERTILIZERS

### R. Navikaitė, <u>R. Paleckienė</u>\*

Department of Physical and Inorganic Chemistry Faculty of Chemical Technology Kaunas University of Technology Radvilenu str. 19 Kaunas, LT - 50254, Lithuania \*Corresponding author, e-mail: <u>rasa.paleckiene@ktu.lt</u>

Humates are now recognized as the single most productive substance in sustainable agriculture. According to scientific literature, the usage of humates stabilizes nitrogen and improves nitrogen efficiency, thereby making it an ideal additive with urea [1-3]. Humates are the only known substance with the ability to hold onto every other nutrient in the soil which enables heightened nutrient absorption. Humic substances (HS) are safe to the environment and all living organisms. A carbon source can be used as a soil amendment, foliar spray and fertilizer enhancer to boost crop production, strengthen root development and improve soil quality. Humates are naturally occurring organic substances found in coal, lignite, shale, claystone and mudstones. Humic substances from different sources have different compositions and biological effects, depending on their chemical structure and physico-chemical properties [2-4].

Peat that can be found in approximately 10 percent of Lithuania's area [5], are great source for extraction of humic substances. Currently, only about 2 % of Lithuanian peat deposits are being exploited, therefore, in this work, the possibility of processing humates chemically is analyzed (production of humic substances from peat their usage together with liquid nitrogen fertilizers-UAN). For this reason, analysis of physical and chemical properties [6] of peat was performed: peats from different peat deposits around Lithuania (10 samples) were compared to each other and their differences and similarities evaluated. The research has shown that the largest concentration of nutrient substances (nitrogen, phosphorus and potassium) is found in peats with highest decomposition degree. The classical fractionation of HS based on differences in solubility at different pH values was performed. Using the AAS method the concentrations of microelements in all samples were measured and it was found that they were different for all samples.

The possibilities of extraction of humates were evaluated by performing experiments with varying testing times and concentrations of KOH. It was found that: optimal fraction of peat:  $\leq 2\mu$ m; ratio of humates to solvent is 1:20; solvent – 0.5 N KOH; duration of extraction: up to 4 hours. The properties, stability and concentration of humic acids in manufactured humic extracts were researched. The concentration of humic acids in the extracts reached 15 to 30 %, while fulvic acids reached up to 1 %. Physical properties and compatibility of humic acid extract with UAN fertilizers were analyzed, stability of the product was evaluated. The product can be deemed stable as observed changes in physical properties after 1 month of evaluation were insignificant.

#### References

1. Hayes, M. H. In Humic Substances: Structures, Properties and Uses (Davis, G. & Ghabbour, E. A., eds), Royal Society of Chemistry, Cambridge, 1998.1-28.

- 2. Yamada, P. et all. Bioscience, Biotechnology, and Biochemistry, **71** (2007) 1294-1305.
- 3. Orrua, M., Übnerc, M., Orrud, H. Estonian Journal of Earth Sciences, **60** (2011) 43-49.
- 4. Saito B., Seckler M.M. Brazilian Journal of Chemical Engineering **31**, 03 (2014) 675 682.
- 5. UTVP/PAF projektas, 2010, <u>http://www.durpynai.gpf.lt/lt/lietuvos-durpynai</u>

6. Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilizers. Official Journal L: No. 304-1, 2003

#### CHANGING PROPERTIES OF UPCONVERTING NaGdF4 NANOPARTICLES

#### K. Paulauskaitė<sup>1</sup>, I. Mikalauskaitė<sup>1</sup>, A. Beganskienė<sup>1</sup>

<sup>1</sup> Institute of Chemistry, Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko st. 24, 03225, Vilnius, Lithuania \*Corresponding author, a mail: karoling paulauskaite@ahf.stud.yu.lt

\*Corresponding author, e-mail: karolina.paulauskaite@chf.stud.vu.lt

Aim of this work was to investigate influence of  $K^+$  ions in conventional NaGdF<sub>4</sub> system. Various studies had been made by doping transition metals [1] additional RE ions [2] in order to affect, enhance luminescent properties of upconverting nanoparticles. However, the use of other alkali metals in upconversion system instead of Na<sup>+</sup> has not been widely explored as a possibility. Therefore, K<sup>+</sup> ions have been taken into consideration because of its different atomic radius and similar chemical properties.

Upconverting nanoparticles NaGdF4: Yb (20%) Er (2%) with additional doping of K<sup>+</sup> ions in concentration range from 0% to 100% were synthesized. From XRD analysis it can clearly be seen that particles were still of pure hexagonal NaGdF<sub>4</sub> crystal phase up to 50% of K<sup>+</sup> doping, having slight shift in 2 $\theta$  angles. With further increase in amount of K<sup>+</sup> ions additional peaks of second phase were observed. Furthermore, when K<sup>+</sup> completely changed Na<sup>+</sup> ions K<sub>0.67</sub>Gd<sub>1.33</sub>F<sub>4.67</sub> was formed. By doping larger K<sup>+</sup> ions into NaGdF<sub>4</sub> the crystal lattice was affected which had influence on overall luminescence efficiency and red to green ratio. The ratio of integrated red (630-685 nm) and green (513-572 nm) emission bands decreased from 5.27 to 1.41 when K<sup>+</sup> concentration has gradually increased. This effect could also occur as an impact of presence of several different crystal phases starting from 50% K<sup>+</sup>. Moreover, upconversion lifetime measurements of blue, green and red emission bands were carried out and lifetime value were calculated. Energy distance between <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> energy levels was determined from temperature lifetime measurements. Relative and absolute sensitivities were also calculated and will be presented in this work.

Introduction of larger  $K^+$  ions into NaGdF<sub>4</sub> matrix creates a new system in upconverting materials with different luminescent properties. Variation of different amount of alkali metal could be a tool to control outcome of luminescent properties.

#### References

[1] T. Cong, Y.D. Ding, J.P. Liu, H.Y. Zhao, X. Hong, Mater Lett, 165 (2016), pp. 59-62.

[2] L.L. Wang, Z.Y. Liu, Z. Chen, D. Zhao, G.S. Qin, W.P. Qin, Opt Express, 19 (2011), pp. 25471-25478.

#### FORMATION AND CHARACTERISATION OF MIXED METALS HEXACYANOFERRATES BASED AMPEROMETRIC GLUCOSE BIOSENSORS

### A. I. Rekertaitė<sup>1\*</sup>, P. Virbickas<sup>1</sup>, A. Valiūnienė<sup>1</sup>

<sup>1</sup>Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko st. 24, LT – 03225, Vilnius, Lithuania. Corresponding author e-mail.: <u>asta.rekertaite@gmail.com</u>

Prussian blue (PB) is a compound which is often named as "Artificial enzyme peroxidase", due to it catalytic property of reducing hydrogen peroxide under low potential conditions [1]. These conditions are thought to be the most progressive for development of oxidase-based biosensors [2]. Low potential maintained during glucose measurement disable reduction of other electrochemically active materials occurring in blood, thus, glucose measurement become more accurate and sensitive [2-3].

Besides Prussian Blue (PB), which is indeed ferric hexacyanoferrate, deposits of different metal hexacyanoferrates (such as copper (II), cobalt (II), nickel (II), etc.) potentially can be also used as an electrocatalytic properties promoting material in development of chemical sensors and biosensors. Multilayers created by coating the electrode with mixed layers of Prussian blue and other metals hexacyanoferrates exhibit some advanced characteristics in comparison with Prussian blue, for example: significantly improved tolerance to alkaline conditions and increased stability in time [4].

During this work earlier proposed electrochemical "single-step" procedure [5] was performed to create amperometric biosensors based on electroactive layers of Fe, Ni and Co hexacyanoferrates, who was deposited in the polypyrrole (Ppy) polymer together with enzyme glucose oxidase (GOx). In the formation of bioselective layers Fe(II) chloride was mixed with Co (II) or Ni (II) chlorides and K<sub>4</sub>[Fe(CN)<sub>6</sub>] in order to synthesized metals (Fe, Ni and Co) hexacyavoferrates who was further entrapped in polypyrrole, during electrochemical polymerisation of pyrrole. During this procedure Ppy/GOx/PB, Ppy/GOx/PB-NiHCF and Ppy/GOx/PB-CoHCF bioselective layers were formed. All materials (salts, glucose oxidase and pyrrole) was dissolved in one solution – that ensured fast and easy formation of bioselective layer accomplished without any additional acidification, which is considered to be harmful to glucose oxidase.

The amperometric investigations in glucose solution and analysis of Scanning Electron Microscopy (SEM) proved the entrapment of metals hexacyanoferrates and glucose oxidase in polypyrrole layer. During investigations of biosensors reduction current of hydrogen peroxide, formed by GOx catalysed glucose oxidation, was registered at 0.05 V vs Ag|AgCl|KClsat, while uncatalised reduction of hydrogen peroxide do not occur on bare graphite electrode until at least -0.45 V vs Ag|AgCl|KClsat [6]. SEM analysis also indicate the existence of Fe, Fe and Ni, Fe and Co ions in Ppy/GOx/PB, Ppy/GOx/PB-NiHCF and Ppy/GOx/PB-CoHCF layers, respectively.

- 1. A. Karyakin, Curr Opin Electrochem 2017, 5.
- 2. A. Karyakin, Electroanalysis, 13, 813 (2001).
- 3. Valiūnienė, P. Virbickas, A. Rekertaitė, A. Ramanavičius. J. Electrochem. Soc. 2017, 164, B781-B784.
- 4. A. N. A. Sitnikova, A. V. Borisova, M. A. Komkova, A. A. Karyakin. Anal Chem 2011, 83.
- 5. A. Ramanavičius, A. I. Rekertaitė, R. Valiūnas, A. Valiūnienė. Sens Actuators B 2017, 240.
- 6. G. Rajendra Kumar Reddy, P. Suresh Kumar. Mater Sci Eng C 2017, 75.

# MAGNETIC PROPERTIES OF ELECTRODEPOSITED Fe FILMS AS POTENTIAL CATALYST WITH INCREASED EFFICIENCY

J. Reklaitis<sup>1,\*</sup>, A. Nicolenco<sup>2</sup>, K. Mažeika<sup>1</sup>, R. Davidonis<sup>1</sup>, K. Varsockaja<sup>1</sup>, N. Tsyntsaru<sup>2</sup>, H. Cesiulis<sup>2</sup>

<sup>1</sup>State Research Institute Center for Physical Science and Technology, Savanoriu 231, Vilnius LT-02300,

Lithuania

<sup>2</sup>Vilnius University, Physical Chemistry Department, Naugarduko str. 24, Vilnius LT-03225, Lithuania \*Corresponding author, e-mail: <u>jonas.reklaitis@ftmc.lt</u>

Fe and Fe-based materials have been recognized as effective catalysts for hydrogen (HER) and oxygen evolution reactions (OER), as well as for degradation of industrial wastewater pollutions such as dyes, pesticides, surfactants, etc. (Fenton reaction) [1]. In this study, compact and smooth Fe films with various thickness (1-10  $\mu$ m) were electrodeposited onto flat copper substrates from an environmentally friendly Fe(III)-based glycolatecitrate bath operated at pH 7. X-ray Diffraction, Mössbauer spectroscopy and Vibrating Sample Magnetometry were used as nondestructive and precise techniques in order to investigate the structure, composition, magnetic and electrical properties of the samples.



Mössbauer spectroscopy showed that the obtained films consist of pure  $\alpha$ -Fe phase. Nevertheless, the magnetic behavior of electrodeposited Fe is different from that observed on bulk materials [2]. Investigated samples exhibited a strong magnetic anisotropy (Fig. 1) with magnetic moment oriented perpendicular to the surface. The obtained ferromagnetic characteristics of electrodeposited Fe films could enable their easy manipulation toward specific locations within polluted wastewater and possibly increase their catalytic efficiency towards OER [3].

Fig. 1. Magnetization curves of Fe sample:  $\parallel, \perp$  indicates orientation of the field applied to sample.

Acknowledgments. Authors acknowledge funding from H2020 project SMARTELECTRODES (No.778357) and project No 09.3.3-LMT-K-712-08-0003.

- H. Zhang, Y. Feng, Y.Cheng, M. Dolors Baró, A. Altube, E. García-Lecina, F. Alcaide, E. Pellicer, T. Zhang, J. Sort, ACS Omega, 2 (2017) 653–662.
- 2. M.T. Johnson, P.J.H. Bloemen, F.J.A. den Broeder, J.J. de Vries, Reports on Progress in Physics, 59 (1996) 1409-1458.
- 3. L. Wang, H. Yang, J. Yang, Y. Yang, R. Wang, S. Li, H. Wang, S. Ji, Ionics, 22, (2016) 2195–2202.

# P 45

#### QUALITY CONTROL OF TRITIUM MEASUREMENTS IN ENVIRONMENTAL SAMPLES

D. Riekstina<sup>1,\*</sup>, T. Krasta<sup>1</sup>, A. Lescinskis<sup>2</sup>

<sup>1</sup>Institute of Solid State Physics, University of Latvia, Kengaraga str.8, LV1063, Riga, Latvia <sup>2</sup>Institute of Chemical Physics, University of Latvia, Jelgavas str. 1, LV1586, Riga, Latvia \*Riekstina, e-mail: oveveris@latnet.lv

Quality assurance of measurement results is of utmost importance for making right decisions in science, industry, environment and food safety control. Tritium (H-3,  $E_{\beta} = 18.6 \text{ keV}$ ,  $T_{1/2} = 12.32$  years) activity determination with a high confidence level is necessary both for radiation safety purposes, and for development of high technologies (in JET nuclear synthesis reactors).

This work presents results of tritium activity analysis in ground water, drinking water and radioactive polluted water samples collected in Latvia. Tritium activity measurements were carried out with the liquid scintillation method (LSC) over a longer period of time. Implementation of the quality assurance system requirements according to the laboratory competence standard LVS EN ISO/EIC 17025:2005L was an essential part of that work. The main procedures which ensure confidence of obtained results are as follows: use of calibrated measurement standards, calibration of measurement instruments, control charts, repeatability (stability) checks, reproducibility of results, uncertainty assessment and participation in intercomparison measurements.

Results of the long-term (since 1997) monitoring [1] of tritium content in water of the decomissioned Salaspils nuclear reactor (SNR, 1961-1998) basins and ground water are presented. Control of drinking water in food industry and urban water-supply was performed according to the regulations No.235 of the Latvian Cabinet of Ministers, adopted in 2003 and Directive 98/83/EC of the EU Council on the quality of water.

Measurements of tritium activity in water samples were carried out with the liquid scintillation spectrometer Packard TRI-CARB 2100 and 2900 using the scintillation liquid OptiPhase "HiSafe"3<sup>TM</sup>. Measurement time was up to 12 hours or until statistical uncertainty less than 2 % was achieved. For that counting time, minimal detected activity (MDA) was 4 Bq/l.

Tritium activity in waters of SNR varied within a wide range (5 - 80.000 Bq/l). The performed monitoring allowed to establish timely the emergency situation related with the water leakage from the storage basin and so to ensure the elimination of possible large scale environmental pollution. The control of drinking water in food industry and urban water taps has shown that the concentration of tritium in measured drinking water samples never exceeds the 10 Bq/l limit.

Participation in the "IARMA Proficiency Test" intercomparison measurements of tritium activity in water demonstrated quality of our analytical results and allowed to identify some potential problems.

#### References

1. D. Riekstina, J. Berzins, T. Krasta, O. Skrypnik, J, Rudzitis, J. Alksnis, Proc. of the 3rd Int. Conf. on Radiation and Applications in Various Fields of Research, 8-12 June, Budva, Montenegro, 2015, 375-380.

### ELETROCHEMICAL ANALYSIS OF ALUMINIUM SURFACE FOR HYBRID BILAYER FORMATION

### T. Sabirovas\*, A. Valiūnienė

Faculty of Chemistry and Geosciences, Vilnius University Naugarduko str. 24, LT-03225, Vilnius, Lithuania \*Corresponding author, e-mail: tomas.sabirovas@chf.stud.vu.lt

Hybrid bilayer lipid membrane (hBLM) is one the model for mimicking plasma membranes [1]. This model is quite attractive, since surface modification, such as self-assembly monolayers, can be easily formed and investigated with various surface techniques. Surfaces such as gold, cadmium stannate [2] or titanium [3] had been used for hBLM formation. In this study aluminium as a substrate was chosen, as it is one the most abundant metals on earth and has uncomplicated preparation of the surface for self-assembled monolayer (SAM) formation.

In this study octadecyltrichlorosilane (OTS) was used as an anchoring unit and vesicle fusion method was applied for hybrid bilayer formation. Vesicles consisted of 1, 2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) and cholesterol (Chol) at molar % ratio 60/40. Contact angle measurements and real-time dynamic fast Fourier transformation (FFT) electrochemical impedance spectroscopy (EIS) was used to analyze formation of the layers. All electrochemical measurements were taken in phosphate buffer solution (0.1 M NaCl, 0.01 M NaH<sub>2</sub>PO<sub>4</sub>, pH 7.1).

After polishing, aluminium plate exhibits hydrophilic properties. After silanization procedure, the surface displays hydrophobic properties, reaching values of contact angle up to  $110^{\circ}$ . An increase of contact angle indicates formation of SAM. This data correlates well with EIS measurements. After forming the SAM, a significant decrease of capacitance was observed: from  $2.32 \,\mu\text{F cm}^{-2}$  to  $1.32 \,\mu\text{F cm}^{-2}$ . Further decrease of capacitance to  $0.62 \,\mu\text{F cm}^{-2}$  was detected after vesicle fusion. This is typical electrochemical behavior well observed on gold surfaces [4] for formation of SAM and hybrid bilayers.

To summarize, the hybrid bilayer formation on mechanically polished aluminium surface was achieved successfully. This could be applied for detection of membrane damaging proteins such as phospholipase A<sub>2</sub>.

- 1. C. W. Meuse S, L. Plant, Biophys. J. 1998, 74 (3), 1388-1398.
- 2. A. Valiūnienė, Ž. Margarian, I. Gabriūnaitė, V. Matulevičiūtė, T. Murauskas, and G. Valinčius, J. Electrochem. Soc. 2016, 163 (9), 762-767.
- 3. A. Valiūnienė, T. Petrulionienė, I. Balevičiūtė, L. Mikoliūnaitė, and G. Valinčius, Chem. Phys. Lipids, 2017, 202, 62-68.
- 4. G. Valincius, M. Vaudin, J. Electroch. Soc. 2001, 148 (8), E341-E347.

#### BIOTECHNOLOGICAL SYNTHESIS OF BIODIESEL FUEL BY INTERESTERIFICATION OF RAPSEED OIL WITH METHYL FORMATE

### <u>I. Sendzikaite<sup>1\*</sup></u>, V. Makareviciene<sup>2</sup>

<sup>1</sup>Kaunas University of Technology, K. Donelaicio st. 73, LT-44249 Kaunas, Lithuania <sup>2</sup>Aleksandras Stulginskis University, Studentu 11, Akademija LT-5336 Kauno r., Lithuania \*Corresponding author, e-mail: ieva.sendzikaite@ktu.edu

Due to the awareness of adverse effects of conventional fuels to environment and to frequent rise in crude oil's price, the need for sustainable and environment friendly alternate source of energy has gained importance. Recently, options have been analysed to replace the triglyceride transesterification process, which is generally used in biodiesel production, by the process where raw glycerol is not generated, whereas triacylglycerides obtained instead glycerol can be directly used as fuel for a diesel engine in a mixture with fatty acid esters. In the present work, interesterification of rapeseed oil to biodiesel was carried out with methyl formate and using lipase as catalyst. Process scheme is shown in figure 1. First, the most effective biocatalyst suitable for the process was selected. 14 different lipases were studied. The samples obtained after the synthesis were analysed by the thinlayer and gas chromatography. Process experiments were performed using a methyl formate to oil molar ratio of 6 to 40, a lipase amount of 5 to 17 % (mass of oil), and synthesis duration of 3 to 48 h. The highest yield of fatty acid methyl esters (FAME) was obtained using Lipozyme RM IM as catalyst and its optimal amount was 13 %. Optimal temperature was found to be 20 °C and duration of interesterification 42 h. Optimal molar ratio of oil and methyl formate was determined 1:32. Under obtained conditions transesterifications degree was 60.68 %.



Figure 1. Scheme of interesterification of oil using methyl formate

# REMOVAL OF Pb<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup> AND CrO4<sup>2-</sup> FROM ELECTROPLATING WASTEWATER BY ELECTROCOAGULATION

### G. Burba<sup>1</sup>, <u>D. Sinkevičiūtė</u><sup>2</sup>, N. Dukštienė<sup>2\*</sup>

<sup>1</sup>AB "Achema", Jonalaukio k., Ruklos sen, LT-55550, Jonavos r, Lithuania <sup>2</sup>Departament of Physical and Inorganic Chemistry, Kaunas University of Technology Radvilėnų pl.19, LT-50254 Kaunas, Lithuania \*Corresponding author, e-mail: nijole.dukstiene@ktu.lt

Effluents issued from surface finishing and electroplating industry usually contain, metal ion concentrations much higher than the permissible levels. Therefore, harmful heavy metal (like nickel, chromium and others) ions contaminating wastewater must be treated before releasing into environment. Among the different methods available to eliminate heavy metals from wastewater, the electrocoagulation is a green and environmental-friendly process and offers many advantages [1-2]. Given that industrial wastewater can contain various different metals, it is necessary to focus on the simultaneous removal of two or more metals and also to quantify the interference of one metal with the other. The synthetic wastewater, which is studied in this paper, was simulated from a real metal plating plant polluted with  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$  and  $CrO_4^{2-}$ . The performance of an electrochemical-reactor with monopolar aluminium electrodes for removing these metal ions was studied to determine the optimum operational conditions. The electrodes were made from used electronic aluminum coolers intended for recycling. The effect of key parameters such as initial metal concentration, number of present metals, charge loading and current



Fig. Variation of metal ion concentration in the electroplating wastewater with time at  $j_a = 25 \text{ mA/cm}^2$ :  $1 - Ni^{2+}$ ,  $2 - Zn^{2+}$ ,  $3 - Pb^{2+}$ ,  $4 - CrO_4^{2-}$ 

density on the electrocoagulation process efficiency were investigated. The experimental results revealed that the removal efficiency of metal ions increases with increasing both electrolysis time and direct current density. Also, it was found that  $\text{CrO}_4^{2-}$ ions removal rate is lowest as compared to other ions under the same conditions. This showed that longer electrocoagulation time is necessary for  $\text{CrO}_4^{2-}$  removal to the admissible level (50µg/l, The European Environment Agency, EC No 166/2006) for effluents discharged into the sewage system.

Over 98% of metal ions were removed efficiently by conducting the electrocoagulation treatment at current density of 25 mA/cm<sup>2</sup> and time of 60–90 min. These operating conditions led to specific energy consumption and specific amount of dissolved electrodes of around 118–168 kWh//m<sup>3</sup> and 2.72–2.77 kg/m<sup>3</sup>, respectively.

- 1. T. M. Zewail, N. S. Yousef, J. Electroanal. Chem., 735 (2014) 123–128.
- 2. D. T. Moussa, M. H. El-Naas, M. Nasser, M. J. Al-Marri, J. Environ. Manage., 186 (2017) 24-41.

### EFFECT OF MANGANESE DOPING ON THE LOW-TEMPERATURE SYNTHESIS OF TRICALCIUM PHOSPHATE POLYMORPHS

# L. Sinusaite<sup>1,\*</sup>, I. Grigoraviciute-Puroniene<sup>1</sup>, A. Antuzevics<sup>2</sup>, A. Kareiva<sup>1</sup>, A. Žarkov<sup>1</sup>

<sup>1</sup>Institute of Chemistry, Vilnius University, Naugarduko st. 24, LT-03225, Vilnius <sup>2</sup>Institute of Solid State Physics, University of Latvia, Kengaraga st. 8, LV-1063 Riga, Latvia \*Corresponding author, e-mail: <u>lauryna.sinusaite@gmail.com</u>

Alpha- and beta-tricalcium phosphates ( $\alpha$ -TCP and  $\beta$ -TCP) raise an interest due to their biomedical applications as injectable bone cements, osteoconductive coatings on metal prosthesis or bulk components for bone repair [1, 2]. Moreover, there are numerous nonmedical applications of TCP polymorphs such as: being catalyst for chemical reactions, host materials for lasers, fluorescent materials, gas sensors, sorbents for a treatment of contaminated soils and water [3]. There are number of studies showing that doping of TCP with Mn ions could improve their bioactivity and bone mineralization [4]. In this work effect of Mn doping on the low-temperature synthesis of TCP polymorphs was demonstrated.

Mn-doped  $\alpha$ - and  $\beta$ -TCP with Mn concentrations ranged from 0 to 5 mol% were synthesized by wet precipitation method using Ca(NO<sub>3</sub>)·4H<sub>2</sub>O, Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> as starting materials. The reagents were mixed at metals to phosphorous molar ratio of 1.5. Obtained precipitates were filtered, washed with distilled water and ethanol, dried in oven at 50 °C overnight and annealed at 700 °C.

The phase purity and structure of synthesized materials were evaluated using X-ray diffraction (XRD), electron paramagnetic resonance (EPR) and infrared spectroscopy (FTIR). Morphology of  $\alpha$ - and  $\beta$ -TCP was investigated by scanning electron microscopy (SEM). Chemical composition of the samples was determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

Both  $\alpha$ - and  $\beta$ -TCP polymorphs were obtained under identical conditions after annealing at the same temperature by varying Mn content in as-prepared precipitates. It was shown that increase in Mn content leads to the formation of beta-TCP, while pure alpha-TCP was obtained without Mn doping, and a mixture of two polymorphs was obtained for intermediate Mn content. Moreover, it was found that doping with Mn ions allows to obtain single-phase beta-TCP at lower temperatures – 700 °C.

- 1. M. Frasnelli et. al. Acta Biomater., **33** (2016) 283-289.
- 2. I. Grigoraviciute-Puroniene et al. Adv. Powder Technol., 28 (2017) 2325-2331.
- 3. M. Sadat-Shojai et al. Acta Biomater., **9** (2013) 7591-7621.
- 4. P. M. C. Torres et al. J. Inorg. Biochem., **136** (2014) 57-66.

#### PECULIARITIES OF GRANULATION OF CHLORELLA VULGARIS ALGAE

# A. Eimontaitė, R. Šlinkšienė\*

Kaunas University of Technology, Radvilenu st.19, LT-50254 Kaunas, Lithuania \*Corresponding author, e-mail: rasasli@ktu.lt

In the upcoming decades, agriculture will have the challenge to provide enough food for a growing world population without having serious impact on environment. Agronomic practices to apply existing mineral fertilizers (primarily containing N, P and K) at the right time, the right place, in the right amount, and of the right composition can improve the efficiency of fertilizers. The smart use of fertilizers is one of the key factors for increasing crop yield, agricultural productivity and food amount provision. Furthermore, ecological processes, such as nutrient-specific interactions in plants and soil, plant-microorganism symbiosis and nanotechnology, have to be exploited to enhance nutrient uptake. It will be necessary to use modern technologies in agroecosystems in order to supply sufficient amount of food and decrease the negative impacts on the environment induced by chemical fertilization. A combination of biotechnology and nanotechnology has the potential to revolutionize agricultural systems and provide solutions for current and future problems [1-4]. This study was conducted to determine under what conditions the granulated algae could be used as bioactive fertilizer.

For comparison algae Chlorella Vulgaris Buxtrade (GmbH, Germany) was used which chemical composition and particles were analysed using different analysis methods: XRF, SEM, X-ray, IR and results were presented earlier [5].

As results show, Chlorella Vulgaris algae agglomerates not easily because it is amorphous material with spherical particles. Therefore, in the granulation process binding materials and additional agglomeration centers should be used, in this case – molasses and recycle respectively. Influence of concentration of molasses solutions and recycle on the quantity of marketable fraction and static strength of algae granules are presented in Figures 1 and 2.



- 1. P. S. Bindraban et.al. Revisiting fertilisers and fertilisation strategies for improved nutrient uptake by plants. Biology and Fertility of Soils, **51(8)** (2015) 897-911.
- M. Calabi-Floody et.al. Smart Fertilizers as a Strategy for Sustainable Agriculture. Advances in Agronomy, 2017. DOI:10.1016/bs.agron.2017.10.003
- 3. S. Ahmad et.al. Effects of Some Major Plant Nutrients on Growth and Yield of Wet Season rise. Journal of Scientific Achievements, **2(4)** (2017) 5-15.
- 4. A. Gallais et.al. The challenge of improving nitrogen use efficiency in crop plants: towards a more central role for genetic variability and quantitative genetics within integrated approaches. Journal of Experimental Botany, **58**(**9**) (2007) 2369-2387.
- 5. A. Eimontaitė, R. Šlinkšienė. Bioactive additives in compound fertilizers. Open readings 2018: 61st international conference for students of physics and natural sciences, Vilnius, 2018, 294.

#### DEVELOPMENT OF POLYMER MEMBRANES FOR CATALYTIC CO<sub>2</sub> ABSORBTION

<u>E. Sprugis</u><sup>1,2,\*</sup>, G. Vaivars<sup>1,2</sup>, J. Kleperis<sup>2</sup>

<sup>1</sup>Faculty of Chemistry, University of Latvia, Jelgavas 1, LV-1009, Riga, Latvia <sup>2</sup>Institute of Solid State Physics, University of Latvia, Ķengaraga 8, LV-1063, Riga, Latvia \*Corresponding author, e-mail: esprugis@protonmail.com

Humanity's long lasting and continued reliance on fossil fuels is the main cause for the significant increase of CO<sub>2</sub> in the atmosphere and, therefore, greenhouse effect [1]. One approach to counter the negative effects due to increased CO<sub>2</sub> emissions could be removal of CO<sub>2</sub> from the atmosphere and converting it into useful carbon based byproducts using electrochemical reduction powered with sustainably generated electricity. Electrochemical reduction of CO<sub>2</sub> can potentially generate several reaction products with similar reduction potentials and thus selective catalyst materials are needed and many have been investigated by researchers [2]. Careful selection of materials is necessary when constructing electrochemical cell used for CO<sub>2</sub> reduction. Among them is a polymer membrane that separates cathode and anode. Several properties of the membrane determines its suitability for use in the electrochemical cell: proton conductivity, gas permeability, mechanical reliability, chemical stability in an aggressive environment. Many polymer materials have been studied and Nafion<sup>®</sup> is still the most widely used material for preparation of proton exchange membranes. Sulfonated poly(ether ether ketone) (SPEEK) is one of proposed alternatives to Nafion<sup>®</sup> due to lower cost and operation at a higher temperature range (100-200 °C). Properties of the SPEEK can be tuned by addition of various modifiers. Ionic liquids (ILs) are suitable for this purpose due to their useful properties (good conductivity, high thermal and chemical stability, as well as the ability to absorb CO<sub>2</sub>[3]) and versatility. However, the mechanical strength of the resulting polymer/IL composite membrines may detoriate significantly depending on the added IL amount, making further adjustments of composition of the membrane necessary. Inorganic nanoparticles, including zirconia based, have been long investigated as an addition to SPEEK polymer membranes due to their positive effect on reducing gas permeation and water swelling [4]. By adjusting the structure of ILs as well as the weight ratio of added IL and inorganic nanoparticles, it is possible to obtain composite membranes with optimal set of properties for use in capturing and electrochemical reduction of CO<sub>2</sub>.

#### References

1. Cook, J.; Oreskes, N.; Doran, P. T.; Anderegg, W. R. L.; Verheggen, B.; Maibach, E. W.; Carlton, J. S.; Lewandowsky, S.; Skuce, A. G.; Green, S. A.; Nuccitelli, D.; Jacobs, P.; Mark Richardson; Winkler, B.; Painting, R.; Rice, K. Environ. Res. Lett. **11** (2016), 048002.

2. Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M. Chem. Soc. Rev. 38 (2008) 89–99.

3. Ramdin, M.; de Loos, T. W.; Vlugt, T. J. H. Ind. Eng. Chem. Res. 51 (2012) 8149–8177.

4. Silva, V. S.; Ruffmann, B.; Silva, H.; Gallego, Y. A.; Mendes, A.; Madeira, L. M.; Nunes, S. P. J. Power Sources **140** (2005) 34–40.

#### SOL-GEL SYNTHESIS OF NEODYMIUM SUBSTITUTED CALCIUM HYDROXYAPATITE

Z. Stankeviciute<sup>\*</sup>, J. Januskevicius, A. Kareiva

Institute of Chemistry, Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko Str. 24, LT-03225, Vilnius, Lithuania \*Corresponding author, e-mail: <u>zivile.stankeviciute@chf.vu.lt</u>

Calcium phosphates are widely applied as biomedical materials, including such uses as bone fillers, bone tissue engineering scaffolds, drug/protein/gene loading and delivery systems, because of their excellent biocompatibility, osteoconductive properties, and similarity to the major biological mineral of human bones. Synthetic calcium hydroxyapatite (CHAP) have attracted extensive interest for potential applications in the biomedical field. Trace elements (Mg<sup>2+</sup>, Sr<sup>2+</sup>, Na<sup>+</sup> etc.) incorporated into CHAP structure could enhance the electrical, luminescence, mechanical strength and biological response.

Biocompatible luminescent materials are fast becoming popular implant material due to their potential clinical applications. Lanthanide-doped CHAP nanoparticles show very interesting luminescence properties, they fluorescence is characterized by narrow emission band widths determined by the lanthanide ions, high photochemical stability and long fluorescence lifetimes (up to several milliseconds). CHAP doped with gadolinium and europium demonstrated significant fluorescence and provide simultaneous therapeutics and fluorescence imaging guidance. Considering the better biocompatibility of CHAP, the present Nd doped CHAP could offer several exciting applications in biomedical area such as infrared imaging, targeted drug delivery and other image guided therapeutic application [1,2].

Samples of Nd substituted calcium hydroxyapatite (Nd:CHAP) were synthesized using aqueous sol-gel method [2]. Nd(NO<sub>3</sub>)<sub>3</sub> hexahydrate was dissolved in dist. water and diluted to 100 mL volume with dist. water. Calcium acetate monohydrate was dissolved in 25 mL of dist. water. Calculated volume of neodymium salt solution was taken and added to a solution of calcium acetate and mixed for 30 min. Complexing agent ethylenediaminetetraacetic acid (EDTA) was dissolved in 25 mL of dist. water and 8 mL of 25 % of ammonia solution. EDTA solution was poured to calcium and neodymium salts containing solution and mixed for 1 hour. Ammonium phosphate was dissolved in 15 mL of dist. water and mixed with calcium, neodymium salts and EDTA containing solution. Solution of ammonia was added until reaction mixture pH was ~11. The temperature of reaction mixtures was increased to 70-80 °C and mixed for 24 hours. After sol formation, reaction mixtures were evaporated and dried for 24 hours at 120°C. Dry gels were heated at 600 °C for 5 hours and twice at 1000 °C for 24 hours, heating rate 1 °C/min. Synthesized samples were characterized using thermogravimetric (TG) analysis, X-ray diffractometry (XRD), scanning electron microscopy (SEM) and Fourier transformed infrared (FTIR) spectroscopy. The microstructure and properties of Nd:CHAP samples were evaluated and discussed.

#### References

1. S. Karthi, G.A. Kumar, D.K. Sardar, C. Santhosh, E.K. Girija. Opt. Mater. 77 (2018) 39–47.

2. K. Gayathri, G.A. Kumar, Solange Ivette Rivera Manrique, C. Santhosh, Dhiraj K. Sardar. J. Lumin. 185 (2017) 180–186.

3. A. Prichodko, F. Enrichi, Z. Stankeviciute, A. Benedetti, I. Grigoraviciute-Puroniene, A. Kareiva. J. Sol-Gel Sci. Techn., **81** (2017), 261–267.

#### STUDY THE SURFACE OF COBALT SULFIDE LAYERS ON POLYAMIDE

#### R. Stokienė, R. Ivanauskas, N. Petrašauskienė

### Department of Physical and Inorganic Chemistry, Kaunas University of Technology, Radvilėnų Str., 19, LT-52254, Kaunas, Lithuania \*Corresponding author, e-mail: <u>ruta.stokiene@ktu.lt</u>

Recently, a growing demand for energy resources has necessitated the development of high performance, environmentally friendly components for storage applications and energy generation [1]. Various chemically synthesized pseudo capacitive materials have been evaluated for their potential applicability as super capacitors. Many researchers have studied the super capacitive properties of various types of metal sulfides such as copper sulfide, nickel sulfide, nickel cobalt sulfide, zinc sulfide, molybdenum disulfide and cobalt sulfide [2]. Among these, cobalt sulfide (CoS) has been considered as one of the most promising and versatile pseudo capacitive electrode materials for super capacitors, solar cells, catalysts, lithium ion batteries and magnetic materials. Cobalt sulfide thin films were prepared by the electrodeposition technique, the chemical bath deposition or modified chemical deposition method [3, 4]. Deposition of cobalt sulfide thin films by successive ionic layer adsorption and reaction (SILAR) method [5].

In this paper, two stages sorption-diffusion technique was employed to deposit the thin film of cobalt sulfide on semi hydrophilic polyamide 6 (PA 6) sheets which served as substrate. In the first stage, polymer samples (500 mm thickness) were sulfurized in 0.002 mol·dm<sup>-3</sup> solution of dodecathionic acid,  $H_2S_{12}O_6$ , the molecules of which contain chains of divalent sulfur atoms,  ${}^{-}O_3S-S_{n-2}-SO_3^{-}$ , up to 6 h at different temperatures. In the second stage, sulfurized samples were treated in 0.16 mol·dm<sup>-3</sup> concentration of Co(II) salt solution for 10 min and at 80 °C. The aim of this study was to investigate the influence of the first stage condition to morphology of formed cobalt sulfide layers on polymer. The surface morphology of these layers was analysed by scanning electron microscopy (SEM), atomic force microscopy (AFM), elemental constitution was to study by energy-dispersive X-ray spectroscopy (EDX) and photoelectron spectroscopy (XPS).

- 1. C. K Ranaweera et al., J. Mater. Chem. A., **4** (2016) 9014–9018.
- 2. R. Zou, M. F. Yuen, L. Yu L, J. Hu, C. S. Lee, W. Zhang, Sci. Rep., 6 (2016) 20264.
- 3. R. Sims, H. Rogner, Energy Policy, **31** (2003) 1315-1326.
- 4. K. Ramasamy, M. A. Malik, J. Raftery, F. Tuna, and P. O'Brien, Chem. Mater. (2010), 22, 4919–4930
- 5. S. D. Sartale and C. D. Lokhande, Indian Journal of Pure and Applied Physics . (2000), Vol. 38, January, p.p. 48-52

### BACTERIAL TOLERANCE TO TOXIC ELEMENTS AND METALS ADSORPTION/METALLOID EXTRACTION IN SOIL AND SEDIMENT HETEROTROPHIC LEACHING SYSTEMS

I. Štyriaková<sup>1\*</sup>, D. Štyriaková<sup>2</sup>

<sup>1</sup>State Geological Institute of Dionýz Štúr, Regional center Košice, Department of Applied Technology for Raw Materials, Jesenského 8, 04001 Košice, Slovakia
<sup>2</sup>Institute of Geosciences, Faculty of Mining, Ecology, Process Control and Geotechnologies, Technical University of Košice, Park Komenského 15, 042 00 Košice, Slovakia
\* Corresponding author, e-mail: <u>iveta.styriakova@geology.sk</u>

The tolerance of soil and sedimentary bacteria to metals and metalloids has been proposed as an indicator of potential toxicity of elements to other forms of life [1]. The purpose of the present test was to verify the tolerance of heterotrophic bacteria to As, Cu, Zn from different environments and to investigate the effect of indigenous heterotrophic bacteria on extraction of toxic elements by bioleaching. The soil was approximately 10 times more contaminated by toxic elements than the sediment, because it originated from the area of the industry source of the metals/metalloids. The presence of metals in the growth medium allowed us to maintain the tolerance of bacteria at polluted environments. The isolates were able to grow in the presence of Cu, Zn, As at concentration higher than 3 mM until 8 mM. Plate counts of indigenous heterotrophs and spore-forming bacteria were determined and showed that spore formed such as *Bacillus* spp. dominated in the soil and sedimentary samples. Only in the sediment sample, the dominant bacterial species tolerant to Cu and Zn belonged to the genus *Pseudomonas. Bacillus* spp. was not tolerant to Cu because these bacteria did not grow on agar plate contaminated with Cu. Bioaugmentation of the soil samples by sedimentary bacteria increased the Zn and As extractions during bioleaching.

The bacterial activity caused the modification of aerobic condition to anaerobic condition and pH change from 6 to 5 during the soil and the sediment bioleaching. The heterotrophic bacteria released Fe with more toxic As metalloid in the field of anaerobic conditions with organic input. The effectiveness of As mobility in soil remediation was also depended from addition of chelators and fertilizers for the activation of tolerant bacteria. This study confirmed the soil and sediment bioremediation effect in Fe, As or Zn releasing efficiency under different leaching conditions. In the batch tests, bioleaching by heterotrophic bacteria of soil and sediment was found to have a higher positive effect on the extractions of Cu, As and Zn. In the column tests, there was a lower positive effect on the extractions of Cu, Zn and As from the sediment and in the case of the soil a lower positive effect on the extraction of Zn and As and a higher positive effect to Cu than in the batch test. The concentration of dissolved Cu in soil leachates was lower in the presence of indigenous bacteria than in abiotic control.

Cu is immobile in samples with heterotrophic bacteria because of its sequestration with organic matter and bacterial metabolites [2]. These results indicated that heterotrophic bacteria can affect the mobilization of Cu and Zn cations from soil and sediment in the presence of organic matter in natural environment as well as in the chemical decontamination processes with the using chelators. The heterotrophic bioleaching is a suitable technology for As removal from the contaminated soil and sediment.

- 1. B. H. Olson, I. Thornton, J. Soil Sci., 33 (1982) 271-277.
- 2. J.U. Navarrete, D.M. Borrok, M. Viveros, J.T. Ellzey, Geochim. Cosmochim. Acta, 75 (2011) 784-799.

# NONAQUEOUS CAPILLARY ELECTROPHORESIS METHOD FOR THE DETERMINATION OF PERFLUORINATED COMPOUNDS

# H. Lees, K. Siilak, P. Saar-Reismaa, M. Vaher

Department of Chemistry, Tallinn University of Technology, Akadeemia tee 15, 12618, Tallinn, Estonia

Perfluorinated alkyl surfactants (PFAS) are highly persistent compounds and therefore ubiquitous in the environment. PFAS are bioaccumulative, potentially toxic and may present risk to human health [1,2]. Among these PFAS, perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the two most commonly found pollutants in the environment. They can be found in very different matrices, e.g. packaging materials, soils, dust, ground and surface water, wastewater, drinking water, sediments, marine wildlife (fish) as well as in human blood.

Nonaqueous capillary electrophoresis (NACE) method with conductivity detection was developed and validated for the determination of perfluoroheptanoic acid (PFHA), PFOA and PFOS in wastewater samples. The baseline separation of these pollutants was achieved in less than 6 min by applying a simple BGE composed of a 0.75 mM MOPS and 1.5 mM TEA dissolved in a mixture of acetonitrile and methanol (50:50, v/v). The method was linear ( $R^2$ >0.996) at concentrations ranging from 2 to 20 µM with method detection limits ranging between 0.5 and 0.75 µM depending on the analyte. Precision tests resulted in maximum RSD values of 1.8% (n=6) and 5.8% (n=6) for the migration times and peak areas, respectively.

The developed NACE method was successfully applied to the analysis of PFHA, PFOA and PFOS in wastewater using solid phase extraction (SPE) for sample purification and concentration. The use of SPE enabled to improve LODs with an enrichment factor of 1000. The developed method is very fast and simple for the determination of PFAS in wastewater.

# Acknowledgements

This work was supported by Estonian Centre of Analytical Chemistry (AKKI).

# References

Giesy K., Kannan J.P., Environ. Sci. Technol., 36 (2002), 147A
 Schultz M. M. et al., Environ. Eng. Sci. 20 (2003) 487

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

### L. Valeikiene, R. Paitian, I. Grigoraviciute-Puroniene, A. Kareiva

Faculty of Chemistry and Geosciences, Institute of Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania

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

In present study, the Mg(X)/Al (X=Ca, Sr, Ba, Ni, Cu, Zn; 10 mol%) 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, TG and FTIR analysis.

- 1. Miyata, S., 1983. Anion-exchange properties of hydrotalcite-like compounds. Clay Clay Miner. 31, 305–314.
- Klemkaite-Ramanauske, K., Zilinskas, A., Taraskevicius, R., Khinsky, A., Kareiva, A., 2014. Preparation of Mg/Al layered double hydroxide (LDH) with structurally embedded molybdate ions and application as a catalyst for the synthesis of 2adamantylidene(phenyl)amine schiff base. Polyhedron 68, 340–345.

# TEMPERATURE INFLUENCE OF HYDROTHERMAL PROCESSING ON PEROXIDE CONTENT AND CRYSTALLINITY OF CALCIUM AND PARTIALLY SUBSTITUTED STRONTIUM HYDROXY-PEROXYAPATITES

#### V. Valkovska<sup>1\*</sup>, A. Osīte<sup>1</sup>, G. Niaura<sup>2</sup>, A. Kareiva<sup>3</sup>

<sup>1</sup>Department of Analytical Chemistry, University of Latvia, Jelgavas Str. 1, LV-1004, Riga, Latvia <sup>2</sup>Department of Organic Chemistry, Center for Physical Sciences and Technology, Sauletekio Ave. 3, LT-10257, Vilnius, Lithuania <sup>3</sup>Department of Inorganic Chemistry, Vilnius University, Naugarduko Str. 24, LT-03225, Vilnius, Lithuania

\*Corresponding author, e-mail: valkovska.valda@gmail.com

Hydroxyapatite is one of the main biomaterials used for clinical applications. The lack of these materials is antibacterial properties that can be improved by substituting calcium with strontium and hydroxyl group with peroxide ion in the HAp structure [1, 2]. Solution of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is suitable for the inclusion of peroxide ions in structure of apatite. H<sub>2</sub>O<sub>2</sub> is mainly used as a biocide for medical and veterinary disinfection and sterilization, as well as for other antimicrobial applications [2, 3]. In the human body phagocytes are generating H<sub>2</sub>O<sub>2</sub> to ensure function of the immune system [4].

In this study we performed investigation of partially strontium substituted hydroxy-peroxyapatites (SrHPerAp) by permanganatometry, X-ray powder diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. Results of incorporated peroxide amounts are shown in Figure 1. There were observed changes in parameters of infrared and Raman bands due to the substitution of the samples or treatment procedure conditions with H<sub>2</sub>O<sub>2</sub> solution. In a previous study [2] it was observed that the incorporation of peroxide in HAp increases the antibacterial activity against of *Pseudomonas aeruginosa* and *Staphylococcus aureus* bacterial strains.



Figure 1. Peroxide content in HPerAp samples, hydrothermally treated with 50%  $H_2O_2$  solution at different temperatures (100 °C-150 °C) for 6 hours

#### References

1. J. Kolmas, E. Groszyk, D. Kwiatkowska-Róhycka, BioMed Research International, 2014 (2014) 1-15.

2. V. Valkovska, A. Osīte, L. Buša, V. Nikolajeva, Key Engineering Materials, 762 (2018) 14-18.

3. G. McDonell, in: PATAI's Chemistry of Functional Groups, John Wiley & Sons, 2014, pp. 1-34.

4. A. Osite, K.A. Gross, A. Viksna, J. Prikulis, A. Sainova, Recent Advances on Mechanics, Materials, Mechanical Engineering and Chemical Engineering, (2015) 75-79.

### TREATMENT OF ANODIZED ALUMINIUM DYEING WASTEWATER BY DRINKING WATER DEIRONING RESIDUALS

# E. Zubrytė<sup>1\*</sup>, A. Gefenienė<sup>1, 2</sup>, D. Kaušpėdienė<sup>1</sup>, S. Jankauskas<sup>1</sup>, R. Ragauskas<sup>1</sup>

<sup>1</sup>Center for Physical Sciences and Technology, LT-10257 Vilnius, Lithuania <sup>2</sup>Lithuanian University of Educational Sciences, LT-08106 Vilnius, Lithuania \* editazubryte@gmail.com

Different types of industries use a wide variety of synthetic dyes with complex aromatic structure. Effluents generated by these industries contain organic and inorganic pollutants. Among the various chemical and physical treatment techniques adsorption and coagulation/flocculation processes have been extensively used for the treatment of colored wastewater [1, 2]. Recently, many attention has been paid to the search for low-cost adsorbents [3, 4]. As coagulation has been found to be efficient and cost effective process [5], the utilization of water treatment sludge for the regeneration of the coagulants has been also proposed [6].

In the present study, eco-friendly waste, i.e., drinking water deironing residuals were used for the treatment of anodized aluminium dyeing wastewater. Theywere collected from a drinking water treatment plant in Vilnius, Lithuania. Chemical composition of amorphous solid waste expressed in the form of main oxides was as follows: 78% Fe<sub>2</sub>O<sub>3</sub>, 7.4% P<sub>2</sub>O<sub>5</sub>, 7.4% CaO, and 5.2% SiO<sub>2</sub>. The action of underground water deironing residuals as adsorbent was combined with the impact of ferric chloride as coagulant. Moreover, acidification of wastewater or partial dissolution of adsorbent with 5 M HCl was carried out to produce a coagulant in-situ in the batch system containing Fe(III) compounds. The experiment was conducted in the laboratory scale using not diluted and diluted wastewater. The dye and aluminium removal ability was investigated by mixing wastewater with varying amount of adsorbent and coagulant. The effect of various parameters such as contact time, initial and final pH, initial concentration of the chromium complex dye and aluminium was investigated. The residual color in the supernatant solution was determined by UV-vis spectrometry (Varian Cary 50). The aluminium, chromium and iron concentrations were determined with an ICP optical emission spectrometer (Optima 7000DV from Perkins Elmer).

Kinetic measurements showed a fast and efficient removal of color and aluminium. Analyses of the filtrate has proved that most of the contaminants were removed within the first 5 minutes. Maximum reduction of color was achieved, and the maximum amount of aluminium was removed when the final pH value of the solution ranged between 4 and 5. The final solution pH highly depends on the amount of all constituents of the system. The results revealed that the optimum solid-liquid ratio 1:40 (w/v) provided the highest color and aluminium removal efficiency of 97% and 99%, respectively.

The obtained results suggest that the investigated process of simultaneous adsorption and coagulation is suitable for the removal of chromium complex dye and aluminium from the aluminium dyeing wastewater.

- 1. M. R. Gadekar, M. M. Ahammed, Desalin. Water Treat., 57 (2016) 26392-26400.
- 2. D. Karadag, S. Tok, E. Akgul, K. Ulucan, H. Evden, M. A. Kaya, Ind. Eng. Chem. Res., 45 (2006) 3969-3973.
- 3. M. M. Hamed, I. M. Ahmed, S. S. Metwally, J. Ind. Eng. Chem., 20 (2014) 2370-2377.
- 4. M. Seredych, T. J. Bandosz, Ind. Eng. Chem. Res., **46** (2007) 1786-1793.
- 5. S. Rana, S. Suresh, Mater. Today:. Proc., **4** (2017) 567-574.
- 6. T. Ahmad, K. Ahmad, A. Ahad, M. M. Alam, J. Environ. Manage., 182 (2016) 606-611.

# **INDEX OF AUTHORS**

# A

Abola	
Aglinskaitė	
Aksamit-Koperska	
Aksimentyeva	
Alinauskas	
Al-Rawajfeh	
Al-Rbaihat	
Al-Sagarat	
Al-Shamaileh	
Ancutienė	
Antuzevics	
Asadauskas	

# B

Bagdžiūnas 40
Bahriychuk 46
Balasubramanian
Balcerbule 69
Balciunas
Balevicius
Barauskienė 41
Barkauskas 49
Barmina73
Barron 14
Bartkevics
Beganskienė 77
Behunova
Bekényiová 42
Blūma 20
Bogans
Bogdanova 30
Brasiunas 43
Briančin 42
Bujňáková 42
Bulska
Burba
Buša 44, 67
Butkutė
С

# 

# D

Dabrilaitė-Kudžmienė 66
Danková 42
Dauksaite 50
Davidonis 79
Demchyna 46
Drobniewska
Drzewicz
Dudarko 47
Dukštienė 64, 83
Dulksnis
Т
E
Eimontaitė
Elsts
Etin
F
Г
Fadlyani74
Furtat
G
Gabriunaite
Gaidukevič
Garnaga-Budrė16
Garskaite
Gavare
Gefenienė
Gešperová
Giebultowicz
Globa
Glumbokaite
Godina
Golubevas
Grebnevs
Grendaitė
Grigoraviciute-Puroniene
Gross
Н
Halicz
I
Inkrataitė 55

Ivanauskas	56,	57,	88
------------	-----	-----	----

# J

Jančaitienė	
Jankauskas	
Jansons	59
Janulevičius	
Januskevicius	
Jaskūnas	66
Jonauske	60
Juodkazytė	

# K

Karasiński       22         Kareiva       37, 45, 52, 60, 74, 84, 87, 91, 92         Karlonienė       61         Karosienė       54         Kasperovičienė       54         Kausaite-Minkstimiene       50         Kaušpėdienė       93         Kępa       44         Kitrys       66         Klimaszewska       63         Kostruba       46
Kareiva
Karlonienė61Karosienė54Kasperovičienė54Kausaite-Minkstimiene50Kaušpėdienė93Kępa44Kitrys66Kleperis86Klimaszewska63Kostruba46
Karosienė54Kasperovičienė54Kausaite-Minkstimiene50Kaušpėdienė93Kępa44Kitrys66Kleperis86Klimaszewska63Kostruba46
Kasperovičienė54Kausaite-Minkstimiene50Kaušpėdienė93Kępa44Kitrys66Kleperis86Klimaszewska63Kostruba46
Kausaite-Minkstimiene
Kaušpėdienė
Kępa44Kitrys66Kleperis86Klimaszewska63Kostruba46
Kitrys
Kleperis
Klimaszewska
Kostruba
Kózka
Krasta
Krata
Krylova64
Kucharski
Kunciūtė 56

# L

Labsvārds	
Laurikenas	
Lazarenko	
Lebed	
Lees	
Leito	
Lescinskis	
Luckutė	

# Μ

Makareviciene	
Mališauskaitė	
Mamaitienė	
Marcinonis	
Matijošius	
Mažeika	
Meile	

Melnyk	27, 47
Mianowicz	
Mikalauskaitė	
Minderytė	
Misevicius	
Mitroová	
Morkan	74
Moskina	
Musiy	46
Myasnikova	73

# Ν

Nałęcz-Jawecki	
Navikaitė	
Niaura	
Nicolenco	
Niedzielski	

# 0

Öpik	
Osipovaitė	
Osipovs	
Osīte	

# Р

Paitian	
Pakalniškis	
Palanisamy	
Paleckienė	
Palinauskas	40
Paulauskaitė	
Petrašauskienė	88
Petrulevičienė	
Pluduma	
Pomilovskis	51, 70
Popov	28, 43, 73
Poškus	
Pugaieva	
Pupienis	
Purmalis	

# R

Rachiy	
Ragauskas	
Ramanauskas	
Ramanaviciene	
Ramanavičius	
Rebane	
Reinholds	
Rekertaitė	
Reklaitis	

Riekstina	80
Romanyuk	46
Ruchajus	66
Rudoviča	69

S

Saar-Reismaa	)
Saaver	
Sabirovas	
Sacevičienė	ļ
Sagimbaeva73	;
Samardokas 57	1
Savadova 54	ļ
Savchyn 73	5
Savickaja71	
Šebeka 71	
Selskis 71	
Sendzikaite	2
Sergeyev	5
Shunkeyev73	5
Siilak	)
Sinkevičiūtė	5
Sinusaite	ŀ
Skaudžius 55, 74, 75	,
Skowronek 65	;
Skruodienė71	-
Sliesarenko 47	1
Šlinkšienė 58, 85	,
Sprugis 86	)
Stankeviciute 37, 74, 87	1
Stokienė	5
Stolyarchuk 27	1
Stonevičius 54	ŀ
Strazds	j
Štyriaková D 42, 89	)
Štyriaková I 42, 89	)
Т	

Tautkus	61
Tekoriene	17
Tomina	27

Torres	
Trusovas	
Tsyntsaru	
Turło	
U	

Udvardi	38
Ulevičienė	57

# V

Vaclavikova	27
Vaher	90
Vaivars	86
Valatka	41
Valeikiene	91
Valiūnienė	3, 78, 81
Valkovska	
Valsiūnas	31
Varsockaja	79
Velusamy	32
Vernickaitė	34
Vičkačkaitė	29
Viksna	53
Vīksna	44, 67
Virbickas	
Vitta	55
W	
Wojciechowski	22
Y	
Yalcin	68
Yang	32, 60

# Z

Žalenkienė	
Žarkov	
Zhanturina	
Zhurinsh	
Zubrytė	
Žukauskas	