Analytical Chemistry



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Report of Contributions

Type: Oral presentation

TEMPERATURE EFFECT ON THE YIELD OF METHANE FROM BOG SLUDGE AND REED RAW MATERIALS

Biogas is a gaseous energy resource that can be obtained by anaerobic fermentation using biomass. The main component of biogas is methane (CH4) and carbon dioxide (CO2), which also includes other gases with certain physical properties. Biogas is a renewable energy resource that does not pollute the environment and the air. Biogas production reduces landfill growth and reduces water and soil pollution. The trend of biogas technologies is improving every time, thus the supply for biogas production is increasing. Capital investment in biogas plants requires relatively low costs. Their use reduces the greenhouse effect, as decomposing products emit CH4 and CO2 gases, which trap infrared (thermal) radiation reflected from the earth's surface [1].

Unlike fossil fuels, biogas is a fully renewable resource because it is produced from biomass. Biogas will not only improve the country's energy balance, but will also make a major contribution to conserving natural resources and improving the environment [2].

The research summarizes information on biochemical processes of biogas production and the parameters that affect the results of its production. The research examines the result of obtaining biogas from bog sludge and a mixture of crushed reed. Particular attention is given to temperature, as a parameter that affects the results of methane and biogas production.

In order to perform the work and obtain biogas, bog sludge from Viļaka region, and bog reeds from Daugavpils Esplanāde park were used in, which were dried and divided into components: stems, leaves, flowers. In order for anaerobic fermentation processes to be possible, digestate from the biogas plant "Skaista", Daugava region, Skrudalienas parish was used. Bioreactor EDF-5.4_2 (manufactured by "Biotehniskais centrs", Latvia) was used for research.

The biogas yield during the bioprocess depends on the effect of temperature, the best results in our study were obtained at a temperature of 40°C. During the experiment, 2.78 L of biogas with an average methane content of 38.7% was obtained from a mixture of bog sludge and crushed reeds. If the content of organic compounds in the sludge was higher, the biogas yield would increase during the process. It is more advantageous to use the raw material mixture for biogas production. The proportion of methane in biogas was the best at a temperature of 38° C – 39.9° , but at this temperature regime the total volume of biogas turned out to be about 15% less. The worst results were obtained at a temperature of 42° C – both in terms of the volume of biogas and the proportion of methane in it.

Primary authors: Mr PUČKINS, Aleksandrs; OSIPOVS, Sergejs

Presenters: Mr PUČKINS, Aleksandrs; OSIPOVS, Sergejs

Type: Oral presentation

DETERMINATION OF LATVIAN HONEY FLORAL ORIGINS USING IRMS, UHPLC-HRMS, ICP-MS, FT IR AND 1H-NMR

Natural bee honey is a sweet product made by honeybees (*Apis mellifera L.*) and it has grown in scientific interest in the past decade. Modern and efficient methods of honey analysis are needed in order to assure products quality. One of many honey quality cornerstones is floral origins determination. Monofloral honey has to be gathered from one major floral source at a certain threshold level, so the presence of other plant interference is inevitable, thus making this a difficult task [1]. To investigate possibilities of Latvian honey floral origins determination, the wide instrumental analysis of isotope ratio mass spectrometry (IRMS), ultra-high performance liquid chromatography-high resolution mass spectrometry (UHPLC-HRMS), inductively coupled plasma-mass spectrometry (ICP-MS), Fourier transform infrared spectroscopy (FT IR) and nuclear magnetic resonance (NMR) methods were performed to 78 natural honey samples obtained from local Latvian manufacturers. The true floral origins for used honey samples were verified by melissopalynology analysis. Additionally, a chemometric approach was performed using principal component analysis (PCA) [2].

The preliminary results show that depletion of δ 15N values might be a useful indicator for heather honey due values were statistically different after ANOVA one way test and PCA indicated characteristics of C and N percentage in proteins to monofloral heather honey. Increased rutin levels were observed to buckwheat honey using UHPLC-HRMS. PCA results of FT IR spectra and ICP-MS showed potential to distinguish buckwheat honey from other floral sources while PCA of binned NMR spectra showed the most diversity of honey floral origins assessment.

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Labsvards, K.D.; Rudovica, V.; Kluga, R.; Rusko, J.; Busa, L.; Bertins, M.; Eglite, I.; Naumenko, J.; Salajeva, M.; Viksna, A. Determination of Floral Origin Markers of Latvian Honey by Using IRMS, UHPLC-HRMS, and 1H-NMR. Foods 2022, 11, 42. https://doi.org/10.3390/foods11010042 Acknowledgments:

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Primary authors: DĀVIDS, Krišs (University of Latvia, Faculty of Chemistry); Dr RUDOVIČA, Vita (University of Latvia, Faculty of Chemistry); Dr RUŠKO, Jānis (Institute of Food Safety, Animal Health and Environment "BIOR"); Mr KLŪGA, Rihards (University of Latvia, Faculty of Chemistry); Mrs BUŠA, Lauma (University of Latvia, Faculty of Chemistry); Mr BĒRTIŅŠ, Māris (University of Latvia, Faculty of Chemistry); Ms EGLĪTE, Ineta (Latvian Beekeeping Association); Ms JEVGEŅIJA, Naumenko (University of Latvia, Faculty of Chemistry); Mrs BODROVA, Marina (University of Latvia, Faculty of Chemistry); Prof. VĪKSNA, Arturs (University of Latvia, Faculty of Chemistry)

Type: Oral presentation

IMPACT OF AMINO ACID CONTAINING FERTILIZER ON ELEMENTAL AND ISOTOPIC CONTENT IN SPRUCE AND PINE STANDS

More than half of the territory of Latvia is covered with forests - 3.4 million ha. And forest areas still continue to increase due to the afforestation of abandoned agricultural, former mining areas, and also by natural forest growth. As a measure to increase the competitiveness of planted seedlings with forest environment vegetation and addition of lacking nutrient elements to improve growth conditions of trees forest soil fertilization may be used.

One of the most essential nutrients in a plant is nitrogen. As fertilizer nitrogen is typically introduced to the soil in the form of its inorganic salts (nitrates or ammonia salts). But some studies show that introducing nitrogen in a form of an organic compound, for example, in the form of amino acid - arginine (arGrow® Granulat, Arevo AB, Umeå, Sweden). Introducing nitrogen in the form of arginine benefits to improved growth and stress resistance, reduces environmental impact, and simplifies cultivation. It also reduces nitrogen leakage from the soil which leads to reduced use of fertilizers.

The experiment was carried out in four research sites - Vacciniosa mel. dry and drained mineral soil and Myrtillosa dry and drained mineral soil type forests. Carbon and nitrogen isotope ratio and elemental content in needle, branch, root, and soil samples from both fertilized and control plots were analyzed.

One of the methods to determine the effect of soil improver or fertilizer on a plant is to use isotopically marked nitrogen fertilizer together with the light-stable isotope ratio mass spectrometry (IRMS). IRMS (Elemental analyzer EA3000 coupled to Nu instruments mass spectrometer) was used for the determination of the N and C mass fraction and N and C isotope ratio. Inductively coupled plasma mass spectrometry (ICP-MS, Agilent 8900 ICPMS QQQ) was used for the determination of 16 micro- and macroelements in studied samples. Chemometric Agile Tool (CAT) together with statistical software program R was used for the evaluation and statistical treatment of obtained data.

The aim of this study was to evaluate the impact of the amino acid (arginine phosphate) containing fertilizer on changes in isotopic and elemental content in Scots pine (Pinus sylvestris L.) and Norway spruce (Picea abies (L.) H.Karst) in studied experimental plots.

After fertilization with an arginine phosphate-containing fertilizer, an increase in the mass fraction of nitrogen in spruce needles and a decrease in the value of nitrogen isotope ratio were observed. In the case of pine seedlings, such a pronounced trend was not observed, which lead to the conclusion that arginine phosphate was not the main source of nitrogen in pine needles. In the second growing season, no significant differences in the nitrogen isotope ratio were observed between fertilized and unfertilized pine samples, but changes in spruce were also observed in the second growing season.

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Primary authors: BERTINS, Maris (University of Latvia); Mr LAZDINA, Dagnija (Latvian State Forest Research Institute 'Silava'); Dr VIKSNA, Arturs (University of Latvia, Faculty of Chemistry); Mrs BUSA, Lauma (University of Latvia, Faculty of Chemistry); Mr DUMINS, Karlis (Latvian State Forest Research Institute 'Silava'); Dr KLAVINS, Maris (Faculty of Geography and Earth Sciences, University of Latvia); Ms ZAKE, Signija

Presenter: BERTINS, Maris (University of Latvia)

Type: Oral presentation

APPLICATION OF WASTEWATER – BASED EPIDEMIOLOGY FOR TRACKING HUMAN EXPOSURE TO DEOXYNIVALENOL AND ENNIATINS

Wastewater - based epidemiology (WBE) is a promising biomonitoring approach with the potential to provide direct information on human intake and exposure to food and environmental chemicals. WBE based on the normalisation method using a population biomarker 5-hydroxyindoleacetic acid (5-HIAA) is the aim of this study. This type of normalization technique has been previously used to detect various other compounds and adjusting different population biomarkers1, but to the best of our knowledge this is the first study tracking human exposure to mycotoxins.

For six weeks (from late June to early August) every working day a wastewater (WW) sample was collected from influent in a sewage treatment plant. Free deoxynivalenol was determined in all WW samples. Based on mycotoxin and 5-HIAA content in the samples an intake of deoxynivalenol and enniatins by the population in Riga was estimated.

The provisional intake of DON by the human population of Riga was estimated at 325 ng/kg b.w. that set by the European Food Safety Authority is in range of chronic dietary exposure (214 - 1014 ng/kg b.w. day) 2.

In worst case scenario (if excretion factors are 5% or lower) the sum of average provisional daily intake of enniatins is 1350 ng/kg b.w. day, indicating a potential risk of chronical exposure.

Primary author: BERZINA, Zane

Co-authors: IKKERE, Laura Elina (Institute of Food Safety, Animal Health and Environment "BIOR", Riga, Latvia); PAVLENKO, Romans (Institute of Food Safety, Animal Health and Environment "BIOR", Riga, Latvia); BARTKEVICS, Vadims (Department of Analytical Chemistry, University of Latvia)

Presenter: BERZINA, Zane

Type: Oral presentation

THE OPPORTUNITIES AND CHALLENGES OF CHEMICAL PROFILING OF HERBAL EXTRACTS USING CHROMATOGRAPHIC ANALYSIS

Medicinal plants have a very complex composition with hundreds of chemical components[1]. With the ever-growing market of herbal medicines, the quality control and safety of these products have become an important issue. The currently used analytical methods provided by pharmacopeias can't provide a comprehensive chemical description of herbal medicines, so recently a chemical profiling method has gained attention[2].

The aim of this study was to determine the opportunities and challenges of chemical profiling of herbal extracts using high-performance liquid chromatography (HPLC) and thin layer chromatography (TLC). Herbal extracts were made from commercially available dried tea samples from four different medicinal plants. Multivariate and similarity analyses were performed both on raw data and data with adjusted retention times.

The main challenge that emerged with HPLC analysis was chromatographic peak shifting, which can be solved by adjusting retention times during data analysis. On average Pearson's correlation coefficient value grew by about 50% for data with adjusted retention times in comparison with raw data. Also, the quality of principal component analysis (PCA) models was significantly better for chromatograms with adjusted retention times.

Chemical profiling is a promising new method for the analysis of herbal extracts. Future research should be conducted with other chromatographic methods to gain a deeper knowledge of the chemical composition of herbal extracts.

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Primary authors: Ms BĀRZDIŅA, Ance (Riga Stradiņš University, Department of Pharmaceutical Chemistry, Dzirciema 16, Riga, Latvia; Baltic Biomaterials Centre of Excellence, Headquarters at Riga Technical University, Kaļķu street 1, Latvia); Mr PAULAUSKS, Artūrs (Riga Stradiņš University, Department of Pharmaceutical Chemistry, Dzirciema 16, Riga, Latvia; Baltic Biomaterials Centre of Excellence, Headquarters at Riga Technical University, Kaļķu street 1, Latvia); Dr BRANGULE, Agnese (Riga Stradiņš University, Department of Pharmaceutical Chemistry, Dzirciema 16, Riga, Latvia; Baltic Biomaterials Centre of Excellence, Headquarters at Riga Technical Chemistry, Kaļķu street 1, Latvia); Dr BRANGULE, Agnese (Riga Stradiņš University, Department of Pharmaceutical Chemistry, Dzirciema 16, Riga, Latvia; Baltic Biomaterials Centre of Excellence, Headquarters at Riga Technical University, Kaļķu street 1, Latvia); Dr BRANGULE, Agnese (Riga Stradiņš University, Department of Pharmaceutical Chemistry, Dzirciema 16, Riga, Latvia; Baltic Biomaterials Centre of Excellence, Headquarters at Riga Technical University, Kaļķu street 1, Latvia); Dr BRANGULE, Agnese (Riga Stradiņš University, Department of Pharmaceutical Chemistry, Dzirciema 16, Riga, Latvia; Baltic Biomaterials Centre of Excellence, Headquarters at Riga Technical University, Kaļķu street 1, Latvia)

Presenter: Ms BĀRZDIŅA, Ance (Riga Stradiņš University, Department of Pharmaceutical Chemistry, Dzirciema 16, Riga, Latvia; Baltic Biomaterials Centre of Excellence, Headquarters at Riga Technical University, Kaļķu street 1, Latvia)

Type: Oral presentation

DIETARY EXPOSURE ASSESSMENT TO PERFLUOROALKYL SUBSTANCES

Per- and polyfluorinated alkyl substances (PFASs) comprise a large group of anthropogenic chemicals which are ubiquitous environmental contaminants. In 2020 European Food Safety Authority (EFSA) established a tolerable weekly intake (TWI) of 4.4 ng/kg bw per week for the sum of four PFASs: perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorohexanesulfonic acid (PFHxS) and perfluorooctanesulfonic acid (PFOS).

Many researchers have attempted to estimate the dietary intake of PFASs in different European countries. These dietary intake assessments were based on the average body weight of 70 kg and the consumption rates from national diet surveys. The tolerable daily intake TDI) limit of 0.63 ng kg-1 b.w.-1 established for the Σ 4PFASs by EFSA was exceeded according to most studies (Fig. 1). Many studies estimated the TDI using a very limited basket of food types, resulting in underestimation as the figures given did not reflect the objective dietary intake of PFAS. Difficulties in comparison of the exposure estimates from different studies appear since there is no consensus whether the observed data should be evaluated on the upperbound (UB) or lowerbound (LB) basis. The exposure is likely underestimated via the the LB approach, whereas it is certainly overestimated via the UB approach. Therefore, to reduce the uncertainties in occurrence data, more sensitive analytical methods or improved analytical protocols should be applied to ensure the analysis of PFASs at occurrence levels that comply with the newly established EFSA TWI of 4.4 ng kg-1 b.w.-1.

Primary authors: ZACS, Dzintars; PASECNAJA, Elina

Type: Oral presentation

BIOACTIVITY ENHANCEMENT OF PEO COATINGS BY INTRODUCTION OF AMORPHOUS CALCIUM PHOSPHATE PARTICLES

Bioactivity is one of the key indicators of implant coating quality of and their suitability in bone disease treatment. In vivo it lies in the ability of a certain material to form strong and stable bonds with living tissues. While for its evaluation in vitro, simulated body fluid tests are the most commonly used, based on immersion of a test sample in the environment with physiological conditions and assessment of hydroxyapatite layer growth rate on its surface [1].

The history of bioactive coatings began right after the rise of implantology and until this time many important discoveries related to their fabrication have been made. Numerous studies were devoted to the application of different bioactive compounds, mainly calcium phosphates, on the metal surfaces, using both the solid particles themselves, as well as indirectly in form of solutions, suspensions and gels [2]. Nevertheless, the search for new, simpler and more rational technologies nowadays remains relevant, opening wide opportunities for still few studied, but promising methods, one of which is plasma electrolytic oxidation (PEO).

PEO is an electrochemical procedure that implies interactions occurring between metallic anode and electrolyte at increased voltages, typically 200 V or higher. Under these conditions, shortlived sparks emerge, which, accompanied by oxygen and heat release, cause resolidification and melting of the anode surface and ultimately lead to formation of porous oxide layer. By adding calcium phosphate particles to the electrolyte, it becomes possible to incorporate them into resulting composite and subsequently modify its physicochemical properties, including bioactivity.

It is believed that the use of crystalline calcium phosphate particles for production of implant coatings is preferred, since the biological form of hydroxyapatite, the main inorganic component of mammalian solid tissues, has a crystalline structure rather than amorphous. Indeed, higher crystallinity is accompanied by better adhesion and proliferation of cells on the surface, as well as by lower coating degradation rate [3]. As a result, researchers when working with well-known coating methods successfully rely on this principle.

Howbeit, the findings of this study allow us to declare that specifically for PEO method utilization of amorphous particles is more expedient, contributing to superior implant coating characteristics against crystalline ones. As confirmed by comprehensive comparison of various physicochemical parameters, it was concluded that amorphous particle incorporation results in calcium-richer bioactive oxide layer. Lower density, less pronounced shape and increased specific surface area are supposed to be the factors that allow these particles to get efficiently incorporated.

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Primary author: Mr GREBŅEVS, Vladlens (University of Latvia, Faculty of Chemistry)

Co-authors: Mr ALTUNDAL, Şahin (University of Latvia, Institute of Atomic Physics and Spectroscopy); Dr VITER, Roman (University of Latvia, Institute of Atomic Physics and Spectroscopy); Dr DULSKI, Mateusz (University of Silesia, Institute of Materials Engineering); Ms WALA, Marta (Silesian University of Technology, Faculty of Chemistry); Mrs LEŚNIAK-ZIÓŁKOWSKA, Katarzyna (Silesian

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University of Technology, Faculty of Chemistry); Prof. VĪKSNA, Arturs (University of Latvia, Faculty of Chemistry); Prof. SIMKA, Wojciech (Silesian University of Technology, Faculty of Chemistry)

Presenter: Mr GREBNEVS, Vladlens (University of Latvia, Faculty of Chemistry)

Type: Oral presentation

CHARACTERISATION OF SUBERINIC ACIDS AND THEIR POTENTIAL APPLICATIONS

Global sustainability challenges prompt the world to modify their strategies and shift from a fossilfuel-based economy to a bio-resources-based one and to the production of renewable biomass chemicals. Different processes exist that allow the transformation of raw biomass into desirable bio-based products and/or energy. Depolymerized suberinic acids can be considered as an alternative resource to develop bio-polyols that can be further used in polymeric material production. Birch (Betula Pendula) outer bark was used as a raw material to obtain the suberinic acids. Birch

outer bark was extracted with ethanol and depolymerized with potassium hydroxide/ethanol solution. By acidifying the filtrate to pH 5.0, 3.0 and 1.0, after washing 1 and 2 times, filtration and drying at 50 $^{\circ}$ C and 130 $^{\circ}$ C, 12 suberinic acid fractions were obtained.

In order to determine the chemical properties of obtained suberinic acid samples, several characteristics were determined – total phenolic content (TPC), acid number, saponification number, epoxy groups and hydroxyl number using potentiometric titration. Two instrumental methods also were developed with GC-MS and SEC-RID. GC-MS analysis was performed with 2 separate sample preparation methods to characterise both monomeric fraction as well as polymeric fraction present in suberinic acid samples.

At pH 1, by increasing the drying temperature of suberinic acids, the relative amount of hydroxy acids increases, but at pH 3 and pH 5 the opposite trend is observed. By increasing the drying temperature and the pH value did not change the relative amount of diacids. At pH 5, the relative amount of aromatic compounds decreased when suberinic acid drying temperature was increased. Samples in addition to monomeric fraction also contained a significant amount of polymeric suberin fraction, which cannot be seen by GC-MS without complete hydrolysis. Therefore, two sample preparation methods were used and GC-MS results compared. It was concluded that after depolymerization, all samples are dominated by hydroxy acids separated from the suberin macromolecule. Suberinic acids were tested in bio-polyol synthesis reaction and results were promising.

Primary author: GODINA, Daniela (Latvian State Institute of Wood Chemistry)

Type: Oral presentation

Qualitative fingerprinting of psychoactive pharmaceuticals, illicit drugs, and related human metabolites in wastewater during the COVID-19 pandemic in Riga, Latvia

Multiple studies have outlined that the COVID-19 pandemic and government interventions to curb the spread of the virus are likely to have an effect on mental health and substance use patterns [1]. In this study, we explored the presence of psychoactive pharmaceuticals, illicit drugs and related human metabolites in 24-h composite wastewater samples that were sampled weekly over the period of twelve months (December 22, 2020 to December 14, 2021) from the central WWTP of Riga, Latvia. The analysis was performed via qualitative suspect screening approach using three separate high-resolution mass spectrometry (HRMS) methods, which relied on reversed-phase liquid chromatography (RPLC), hydrophilic interaction liquid chromatography (HILIC) and direct infusion HRMS.

In total, 39 out of 149 substances were detected throughout the sampling period, including pharmaceuticals (e.g., antiepileptics, antidepressants and antipsychotics), illicit drugs (e.g., MDMA, cocaine, amphetamine, etc.) and new psychoactive substances (alpha-PVP). The data were evaluated in relation to COVID-19 incidence rate and the extent of containment and closure policies. For some compounds we observed temporal changes that may be potentially linked with the consequences of the pandemic. For instance, higher detection rates were observed for some illicit drugs during periods, when restrictions on public events were relaxed.

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Primary authors: PERKONS, Ingus (Institute of Food Safety, Animal Health and Environment "BIOR"); Dr PUGAJEVA, Iveta (Institute of Food Safety, Animal Health and Environment "BIOR"); Dr IKKERE, Laura Elina (Institute of Food Safety, Animal Health and Environment "BIOR", University of Latvia); Ms SUKAJEVA, Veronika (Institute of Food Safety, Animal Health and Environment "BIOR")

Presenter: PERKONS, Ingus (Institute of Food Safety, Animal Health and Environment "BIOR")

Type: Oral presentation

DISCRIMINATION BETWEEN CONVENTIONALLY AND ORGANICALLY FERTILIZED GRAINS BY FTIR AND 1H NMR SPECTROSCOPY COMBINED WITH CHEMOMETRICS

In the last decade, the world has seen growth in interest about the food traceability. This includes not only origins of the food, but also, it's accordance to labelling [1]. In this study the authors researched the possibility of using FTIR and 1H NMR spectroscopy in combination with chemometric approach to distinguish between conventionally and organically fertilized cereal grains.

Organically and conventionally fertilized barley and triticale grains were analysed in this study. The samples were obtained at Institute of Agricultural Resources and Economics, Priekuļi Research Centre. For both conventionally fertilized barley and triticale a complex synthetic fertilizer was used. And for biologically fertilized grains, green manure of peas and red clover (T. pratense) for barley and triticale, respectively, was incorporated into the soil.

Both FTIR and 1H NMR spectra showed little or no significant difference between the organically and conventionally fertilized cereal grains. The FTIR spectra showed broad peaks, corresponding to the starch content in the grains. Also, several peaks at 1747 and 2888 cm-1 were observed that correspond to the protein content in the grains. The main peak shifts in 1H NMR spectra were observed at 3.69 ppm, 6.27 ppm, 6.90 ppm, 7.28 ppm, 7.52 ppm and are corresponding to ferulic acid. Less intense chemical shifts were observed also for cinnamic acid, p-coumaric acid, caffeic acid and sinapic acid.

For further analysis, the obtained data were investigated using chemometrics – principal component analysis (PCA). After applying the PCA to the data of FTIR spectra, it was concluded that a signal at 1738 cm-1 and 1750 cm-1 is specific only for the conventionally fertilized triticale and barley grains, respectively. This peak is characteristic for the amino acids in cereal grains and can be explained by the higher protein content in conventionally fertilized cereals. Regarding the treatment of 1H NMR spectra with PCA, it was concluded that the chemical shifts of ferulic acid (in the organically grown barley and triticale grains were more intense and could be used to discriminate between cereal grains from different fertilization regimes.

Primary authors: VIKSNA, Arturs (University of Latvia, Faculty of Chemistry); Ms TARANDA, Karīna (University of Latvia, Faculty of Chemistry); BUŠA, Lauma (University of Latvia, Faculty of Chemistry); KLŪGA, Rihards (University of Latvia, Faculty of Chemistry)

Type: Oral presentation

Isolation of four tocotrienol homologues and plastochromanol-8 from plant oils and the rapid 'green' analysis of nine tocochromanols in cold-pressed plant oils via superficially porous particle packed column technology and supercritical fluid chromatography.

In the present study, four tocotrienol (T3) homologues and plastochromanol-8 (PC-8) were isolated from plant oils; *Linum usitatissimum* (PC-8), *Bixa orellana* (γ -T3 and δ -T3), and *Triticum spelta* bran (α -T3 and β -T3) by supercritical fluid chromatography (SFC). The optimized method of tocopherols, tocotrienols, and PC-8 separation via SFC with UV detection was validated on a biphenyl coreshell column. The sample preparation conditions of the plant oils involved a simple dilution in 2-propanol (1:9, v/v), followed by the direct injection into the SFC. A final assay was developed that facilitated the rapid (<15 min) and sensitive (limit of detection within the range of 2.5–7.4 µg/mL and the limit of quantitation within the range of 7.7-22.6 µg/mL) analyses of tocochromanols in obtained cold-pressed oils from twenty-four different plant species. Furthermore, the method was repeatable and reproducible with % RSD values in the context of standard retention times which ranged within 0.10-0.31 intraday and 0.59-0.79 interday.

Primary author: BASKIROVS, Georgijs

Co-author: Dr GORNAS, Pawel (APP "Dārzkopības institūts", vadošais pētnieks)

Presenter: BASKIROVS, Georgijs

Type: Oral presentation

SYNTHESIS OF IRON HEXACYANOFERRATE IMOBILISED ON CELLULOSE ACETATE FOR CAESIUM SORPTION FROM AQUATIC ENVIRONMENTS

The present study aims development of iron hexacyanoferrate (PB) cellulose acetate (CA) sorbent for the removal of radioactive caesium, rubidium, and thallium from contaminated water environments. The synthesis of PB-CA sorbent conducted by ultrasound assisted micro nozzle technique provided in situ immobilisation of sorbent particles on chemically cleaned of non-used cigarette butt fiber materials. The experiments were provided in freshwater aquariums at laboratory, by using Cs-133 chloride as the model substance added to the aquarium water

The experiments of Cs accumulation studies were provided in the ecosystem containing Ceratophyllum submersum and Pomacea bridgesii and PB-CA sorbent added to the water filtration system. Obtained results showed that despite the presence of PB as a sorbent, still notable accumulation of Cs occurred also in plants Ceratophyllum submersum and living organisms Pomacea bridgesii. In the process of this study 95% of introduced Cs was accumulated on PB while 3% was accumulated in Ceratophyllum submersum and 1% in the flesh of Pomacea bridgesii.

During these studies sorption capacity of used PB sorbent was evaluated and was equal to 17.8 mgCs/gPB. The sorbent capacity is comparable to that reported in the studies [1] indicating effectiveness of the developed sorbent for Cs removal from the contaminated water.

Obtained experimental data allowed to characterise kinetic model of Cs sorption on PB. The experimental data corresponded to the Lagergren's pseudo-second order kinetic model and can be characterized with sorption capacity at equilibrium which corresponds to 25 mg/g.

Primary authors: Mr GRINBERGS, Andrejs; Prof. VIKSNA, Arturs; Mr REINHOLDS, Ingars; EIS-MONTS, Ugis; Ms SALENIECE, Kristine; Mr BERTINS, Maris; Mrs MUTER, Olga

Presenter: EISMONTS, Ugis

Type: Oral presentation

INVESTIAGTION OF NANOSTRUCTURED Bi2Se3 THIN FILMS AS ANODES FOR AQUEOUS RECHARGEABLE LITHIUM-ION BATTERIES

In the last decade, lithium-ion batteries (LIBs) have dominated the world as the most efficient electrical energy storage device. In comparison with lead-acid or carbon-zinc batteries LIBs have a supreme energy density (>200 Wh kg-1), cycle life (up to 3000 cycles), and energy efficiency (>95 %). Despite their huge advantages, however, the use of non-aqueous electrolytes (e.g., LiBF4, LiPF6) is still considered to be a serious drawback of LIBs, as they are flammable, and can be unfriendly to the ambient environment. To solve these shortcomings, the alternative way is to use aqueous electrolytes (e.g., LiNO3, Li2SO4). The first concept of aqueous rechargeable lithium-ion batteries (ARLIBs) was demonstrated in 1994 by Dahn and his research group by showing a possible perspective of the application of lithium aqueous electrolytes. Bi2Se3 is a unique material with a layered structure that has already shown great promise as an anode in LIBs.

This research demonstrates the investigation of the electrochemical properties of Bi2Se3 thin films with formed solid electrolyte interphase (SEI) and Bi2O3 layer. As an electrolyte 5 M LiNO3 was used which is more electrochemically stable than Li2SO4 and LiCl. Bi2Se3 thin films were synthesized using physical vapour deposition. In this work was applied different electrochemical measurements techniques (cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and charge/discharge) to investigate the electrochemical properties.

The analysis of Bi2Se3 thin films in the lithium aqueous electrolyte was investigated for the first time to show the perspective application as anode for ARLIBs and the difference of electrochemical properties between formed SEI and Bi2O3 layer. Results of this work demonstrated that Bi2Se3 thin films with formed SEI layer (Li2O and Li2CO3) on the electrode surface ensure high diffusivity of Li+, high electrochemical stability, and high capacity up to 100 cycles.

Primary author: LAZARENKO, Vitālijs (Institute of Chemical Physics, University of Latvia)

Co-authors: RUBLOVA, Yelyzaveta (Institute of Chemical Physics); MEIJA, Raimonds (Institute of Chemical Physics, University of Latvia); ANDŽĀNE, Jana (Institute of Chemical Physics); VOIKIVA, Vanda (Institute of Chemical Physics); VĪKSNA, Arturs (University of Latvia, Faculty of Chemistry); ERTS, Donāts (Institute of Chemical Physics, University of Latvia, University of Latvia, Faculty of Chemistry)

Presenter: LAZARENKO, Vitālijs (Institute of Chemical Physics, University of Latvia)

Type: Oral presentation

SEPARATION OF BLACK ALDER BARK EXTRACTS USING SOLID PHASE EXTRACTION TO OBTAIN FRACTIONS WITH IMPROVED PROPERTIES

Black alder bark (Alnus glutinosa) refers to the lignocellulosic biomass which together with the main cell wall components contains a wide range of polyphenolic extractives including diarylheptanoids which are recognized as a natural antioxidants [1]. Therefore, black alder bark extract is a resource with wide range of possible practical application including antioxidative additives in cosmetics, or/and as a technical antioxidant in polymeric chemistry. In this way microwave assisted water extraction of black alder bark revealed itself as a fast and energy effective methods of extractives isolation. To increase the antioxidative properties of isolated products via increasing of polyphenolic concentration in them the Solid Phase Extraction (SPE) was utilised with two different sorbents of different polarity (Amberlite XAD2 and Amberlite XAD7).

Figure 1. Process workflow for extract fractionation using solid phase extraction

This approach allowed successfully fractionate black alder bark extract with total mass recovery being 95%. Obtained water fractions were enriched with carbohydrates, while obtained ethanol (EtOH) fractions were enriched with phenolic type compounds and showed higher antioxidative activity comparable to that of non-fractionated extracts.

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Primary author: PALS, Matiss (Latvian State Institute of Wood chemistry)

Co-authors: Dr LAUBERTS, Maris; Dr PONOMARENKO, Jevgenija; Dr ARSHANITSA, Alexandr

Presenter: PALS, Matiss (Latvian State Institute of Wood chemistry)

Type: Oral presentation

Recent trends in pesticide analysis by two-dimensional liquid chromatography - mass spectrometry

Pesticide residues and their degradation products can persist on harvested food, as well as in the environment, therefore representing a risk to human and animal health and the environment. The challenges for the pesticide residue analysis are the huge number of possible residues, the chemical diversity of the pesticides, the variety of matrices, and the control of the statutory maximum residue levels that are partly very low [1].

Classical one-dimensional liquid chromatography - mass spectrometry approaches do not always provide the resolving power and selectivity necessary for the analysis of complex samples. To this end, two-dimensional liquid chromatography - mass spectrometry offers a better resolving power and peak capacity and allows decreasing matrix effects as a result of the advanced separation of analytes and matrix components. Furthermore, two-dimensional liquid chromatography - mass spectrometry allows omitting the classical liquid-liquid and solid-phase extraction steps during sample preparation for some samples [2].

Recent developments in pesticide analysis by two-dimensional liquid chromatography - mass spectrometry could be divided in three large research directions.

Firstly, the aim of the researchers is to simultaneously identify as many different pesticides, for example, QuEChERS amenable and highly polar ones and other food contaminants like mycotoxins, plant growth regulators, alkaloids in different matrices within a single analytical run. By means of using two-dimensional liquid chromatography - mass spectrometry it also becomes more viable to analyse complicated and dirty matrices such as hops, tea and tobacco which used to be quite complicated due to matrix interference.

Secondly, the task of the researchers is to separate and quantify enantiomers of chiral pesticides that have similar physical and chemical properties, but differ in their toxicity and biological activity, because biotransformation of chiral molecules could be stereoselective. Likewise, enantiomers could have different degradation patterns in the environment [3].

Thirdly, the desire of the researchers is to replace classical QuEChERS protocol-based sample preparation with two-dimensional liquid chromatography - mass spectrometry as the only tool of sample analysis and preparation without any further manual sample pre-treatment except extraction with, for example, acetonitrile or acetonitrile - water mixture.

Primary authors: JANSONS, Aris; BARTKEVICS, Vadims (Department of Analytical Chemistry, University of Latvia)

Presenter: JANSONS, Aris