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Abstracts

IL 1

PETROLEOMICS: SPECIATION AND CHEMICAL COMPOSITION OF PETROLEUM CRUDE OIL BY FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY

Alan G. Marshall[1,2],*, Martha L. Chacon Patino[1], Yuri E. Corilo[1,3], Christopher L. Hendrickson[1,2], Logan C. Krajewski[2], Sydney F. Niles[2], Jonathan C. Putman[2], Steven M. Rowland[2,3], Donald F. Smith[1], Chad R. Weisbrod[1],and Ryan P. Rodgers[1,2,3]

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FT-ICR MS offers 10-100 times higher mass resolving power than any other mass analyzer, and is thus the mass analyzer of choice for complex mixture analysis. Accurate (sub-ppm) mass measurement yields elemental composition, numbers of N, O, and S (hetero) atoms (i.e., compound „class"), number of rings plus double bonds (DBE, or „type"), and carbon number distribution (yielding the degree of alkylation)for molecules up to ~1,500 Da. We have assigned more than 125,000 peaks in a single petroleum 9.4 T FT-ICR mass spectrum. Data may be visualized from various graphical images scaled according to ion relative abundance: e.g., class distribution, Kendrick plot, van Krevelen plot, DBE vs. Carbon number, etc.

Petroleomics aims to correlate and ultimately predict petroleum properties and behavior based on its detailed chemical composition. Applications include production deposit characterization, crude oil fingerprinting, crude oil compositional comparisons, heavy ends and asphaltene characterization, identification of naphthenic acids in crude oil and bitumen, biodegradation indices, emulsion stability, and polar compound speciation in the distillation process. This talk will report recent petroleomics technique developments, including imprinted polymers to extract naphthenic acids, and on-line LC FT-ICR MS at 21 tesla (highest field for ICR)) applied to characterization of crude oil and oil spills.

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IL 2

WONDERFUL ADVENTURES OF MASS SPECTROMETRY IN MARVELOUS MACONDO

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A reporter travels around the world with his camera. An analytical chemist, on his journey, would like to take eventually a chromatograph or a mass spectrometer to go to the country of Magical Realism –as García Márquez, the Nobel Prize for Literature, called Colombia. How would the traveling researcher perceive the country, what would be found, and what "images" would be taken? In the presentation, we will make a short but intense expedition through Colombia, an exotic, tropical country with thousands of surprises, and we will see it through a prism of a mass spectrometer visiting different "cities" of interest, Biodiversity and Biomarkers, Alkaloids and Pesticides, and other places.

Biodiversity and secondary plant metabolites. Colombia is one of the most biodiverse countries in the world. The analysis of dozens of tropical flowers (LC-MS with HR-TOF and Orbitrap Mass Analysers) will discover many bioactive substances, flavonoids, anthocyanins, phenylpropanoids. The chemical composition correlates with their intense colours and diverse biological activities. In the floral fragrances of more than fifty plants studied, *ca.* 400 compounds are detected, using HS-SPME monitoring and GC-MS, GCxGC-HRMS analysis, they are present in different proportions and amounts, and their composition changes quickly during the day, attracting pollinators or defending the plant from their enemies. However, not all flowers smell exquisitely, there are exceptions. *Stapelia 2igantean* (Apocynaceae family) flowers of starfish plant (carrion plant) make only friends with coprophilous or necrophilous insects, and have scent that urge us to run away...

Alkaloids and their role in plants. During our trip, we also discover the most toxic alkaloids on our planet, *i.e.* pyrrolizidine alkaloids (PA), isolated by matrix solid-phase dispersion (MSPD) from tropical plants of the genus *Crotalaria* spp. (Fabaceae family), and analysed by GC-MS and UHPLC-ESI$^+$-Orbitrap-MS. The Pas discover a vast variety of structures (*ca.* 600) and forms (bases and N-oxides). For their identification, linear retention indexes (LRI, GC-MS), mass spectra (EI, 70 eV) and, in the case of N-oxides (PANOs), positive ion electrospray are used, accompanied by the fragmentation of protonated molecules, MH^+, induced by collisional activation at different energies, and by the measurement of ion masses with accuracies less than 0.3 ppm. It is incredible how the *Crotalaria* plants "learned" to survive, synthesizing toxic Pas and PANOs in large amounts, since there is a single specialist insect *Utetheisa ornatrix* (Lepidoptera: Erebidae), member of the tiger moth family (Arctiidae), able to eat this plant and, of course, with an additional interest, not only food. *U. ornatrix*, specialized insect on *Crotalaria* species, sequesters plant-derived Pas as protective chemicals (co-evolutionary adaptation), to advertise their unpalatability to potential predators by conspicuous warning coloration (aposematic signals). In addition, the insect transforms PA alkaloids of the plant into new substances (**Figure 1**), which are pheromone precursors *(hydroxydanaidal)* of moths.

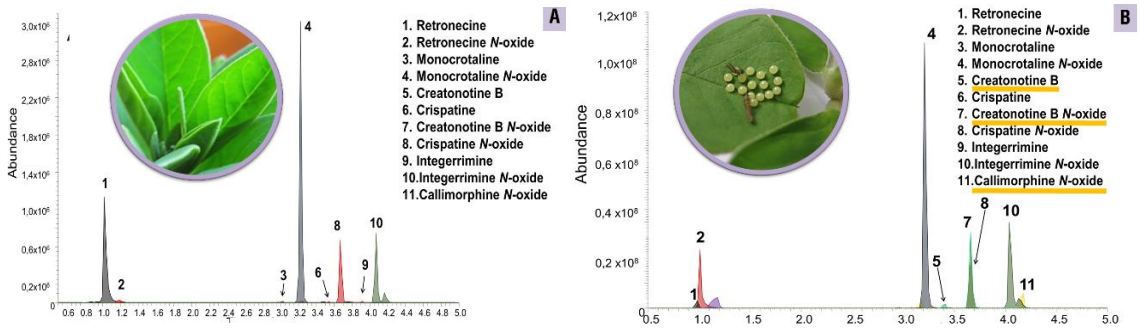

Figure 1. UHPLC-ESI⁺-Orbitrap-MS. Pas and PANOs alkaloids isolated by MSPD method from: **A.** *Crotalaria nitens* leaves. **B.** *Utetheisa ornatrix* eggs.

Different alkaloids are synthesized in tropical plants as a strategy for adaptation and survival; among them, we found *tropane* alkaloids in *Erythroxilum* spp. (Erythroxylacea family) and in *Brugmansia* spp. (Solanaceae family) flowers; *harmala* alkaloids are present in the magical religious ayahuasca or yage, from *Banisteriopsis caapi* (Malpighiaceae family) lianas. The high selectivity of LC-ESI⁺-Orbitrap-MS allows to quantify sensitively both alkaloids and their biotransformation products in plants and in biological fluids, obtained after the ingestion of yage infusions.

Contamination, adulterations and control substances. Colombia, an agricultural industrial country, has large areas of coffee, palm oil, rice, sorghum, cocoa, fruit, and vegetable crops. The use of pesticides –although controlled- in some cases, can cause serious ecological problems. Using GC-MS and LC-MS analytical systems, we could clarify why a severe damage in tomato crops had occurred. It was an adulteration with 2,4-D (systemic herbicide) of the commercial product based on *kasugamycin* (aminoglycoside antibiotic), traditionally used for prevention of tomato crop infection.

The sharp "eye" of the mass spectrometer does not miss the presence of adulterants in several over-the counter drugs sold as "naturists", which have been counterfeited with substances not declared on the label (*e.g.,* with diclofenac and corticoids). Using GC-MS, GCxGC-HRMS and LC-MS we obtained profiles of controlled substances derived from *Cannabis* (>400 samples) and of crude coca extracts (*basucos*). The combination of these analytical techniques allowed, using PCA, to classify confiscated drugs and *Cannabis* products, according to their purity and, in several cases, their origin.

Colombia is a happy country, with good music, beautiful dances and parties. The typical alcoholic beverage is *aguardiente*. Using the derivation of volatile aldehydes (mostly, acetaldehyde) with pentafluorophenylhydrazine (PFPH) placed directly on the SPME fibre, we monitored, as a function of time, the breath of several volunteers after they had been taking different alcoholic drinks (*aguardiente*, brandy, rum, wine or beer). Interestingly, the amount of acetaldehyde in human breath after alcohol beverage taking was like that found in volunteers submitted to 48-hour fasting. On-fibre derivatization with PFPH was also used for the study of air in shoe factories, car exhaust, in overheated cooking oil, and in human sweat.

Petroleum. The gas chromatography technique with a triple quadrupole mass detection system (GC-QqQ-MS) was an excellent tool for looking at the entrails of crude oil and its origin through the biomarkers which we analysed in the saturated fraction isolated from different petroleum and rock samples. MSPD in combination with zeolites as a clean-up system, was used to isolate *n*-paraffins from the extract, which allowed to increase sensitivity and confidence on the detection and identification of hopanes, steranes, terpanes, and other biomarkers in the saturated fraction isolated from petroleum.

With the mass spectrometer in hand, during this very short trip, we discovered different and interesting applications in daily life and in various activities in Colombia, a country of magical realism.

KN 1

COMPOUND SPECIFIC ISOTOPE ANALYSIS – NEW CHALLENGES IN ENVIRONMENTAL AND FOOD STUDIES

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Compound Specific Isotope Analysis (CSIA) holds the potential to reveal new insights into the nature, sources and transformation processes of organic compounds including pollutants in the environment and their mobility in ecosystems, food and human health. Determination of isotopic composition of light elements such as C and H at the molecular and atomic levels provides another dimension of information on organic compounds to supplement knowledge of their chemical identity and their concentration.

This presentation deals with the use of CSIA in environmental and food studies. First, the theoretical background will be presented followed by the review of current limitations and analytical challenges associated with low concentrations, high polarity of organic compounds and potential isotopic fractionation of the target compound. Selected applications and examples in the environment will include the use of CSIA in: (i) source apportionment in natural processes and environmental contaminants such as polycyclic aromatic hydrocarbons and hormones; (ii) elucidating reaction mechanisms and transformation processes including pesticides. The application of CSIA in food science will include the use of isotopes to distinguish natural versus synthetic origin of ingredients. Indeed, cheap, synthetic, petroleum-derived compounds usually have different isotope values than their costly, natural counterparts.

KN 2

COMPREHENSIVE STEROIDS ANALYSIS USING GC×GC-TOFMS

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Identification and quantitation of steroid metabolites in biological samples is essential for the screening of various hormonal disorders. Many of these metabolites are closely related isomers and cannot be easily separated by LC or one dimensional GC due to their chemical and structural similarity. This complicates analysis and impacts reliable analyte assignment. It is important to develop fast and reliable multi-analyte profiling methods for analysis of steroid panels from a single sample. Comprehensive two-dimensional gas chromatography (GCxGC) coupled to a TOFMS provides enhanced chromatographic separation, sensitive detection and reliable identification of the analytes of interest.

Thirty three steroid standards from different classes were combined, derivatized and analyzed using GCxGC-TOFMS to create accurate mass libraries for reliable identification and to develop an efficient separation method. The standards were also spiked into urine and derivatized to evaluate detection in the complex matrices. Initially, the analysis was conducted using high resolution TOFMS coupled to GC×GC. High mass accuracy data along with increased peak capacity of GC×GC allowed for the reliable identification of all 33 spiked steroids. Nominal resolution GC×GC-TOFMS was also used to analyze the same samples since it would be more practical for application in clinical laboratories.

Preliminary data clearly demonstrated successful GC×GC separation of all 33 steroids in urine matrix in about 20 minutes run. Both, high resolution (R>25,000) and nominal resolution (R>1000) TOFMS, instruments are capable of fast data acquisition speeds matching 2D GC requirements without any data loss. Automatic deconvolution of the co-eluting or closely eluting derivatized compounds can be a challenge, as their major mass spectra features can be very similar, thus chromatographic separation is necessary, even when using HRMS. The GC×GC data examples will be shown from both instruments demonstrating critical separations of isomers and chemically similar analytes, separation of which would be practically impossible with one-dimensional chromatography.

O-PETRO 1

THE USE OF MICROEMULSIONS FOR THE EXTRACTION AND SIMULTANEOUS PRE-CONCENTRATION OF PERSPECTIVE CHEMICAL MARKERS FOR IDENTIFICATION OF HYDROCARBON FIELDS

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Today the development of new techniques in the elicitation and identification of hydrocarbon chemical markers is of current interest. The key point of this study is to find out new analytical approaches of more selective (or group quantitative) extraction of trace amounts of chemical markers from oil.

The elicitation of chemical markers is the priority goal for the identification of hydrocarbon deposits and the assessment of their catalytic maturity. But in most cases, it was only possible to state about group analysis without description of specific chemical structures. Moreover, signals from mixture of various compounds, which belong to different classes, were considered as individual compounds. It may distort and depreciate the interpretation of the results of chemical analysis. In addition, it means that numerous markers remain unexplored and those compounds or derived indices, which were considered as markers, may actually be false.

The main point of this work is the application of liquid nanostructured systems - “microemulsions” - as new extractants in the analysis of oil chemical markers. They possess unique properties in comparison with micellar media: ultralow interfacial tension, large interfacial area, thermodynamic stability and the ability to solubilize otherwise immiscible liquids due to their combination of hydrophilic and hydrophobic phases.

Thus, described above characteristics of microemulsions can be used in the analysis of complex mixture of substances such as petroleum. They provide an opportunity of more selective or sometimes group quantitative extraction of chemical markers from the objects. Moreover, the following decomposition of microemulsions before the injection to the chromatograph or other analytical devices lead to the significant concentration (approximately 1-2 orders of magnitude) of the target substances. It may increase the sensitivity of determination of new and existing chemical markers.

The work was carried out with financial support of the Russian Science Foundation (RSF) grant 16-13-10079.

O-PETRO 2

POLYCYCLOALCANE HYDROCARBONS IN TARIBANI OIL

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The presented report contains results of GC-MS studies of C_{10}-C_{16} polycycloalkanes obtained from 200-250°C and 250-350°C fractions of paraffin oil from Taribani deposit of Georgia. Concentrates of polycycloalkanes were isolated by means of distillation, adsorption chromatography on silica gel, triple thermo-diffusion, and extraction with thiocarbamide. The fractions 8-10 obtained by thermo-diffusion represent concentrates of bi-, tri- and tetracycloalkane hydrocarbons from fraction 200-250°C and tri-, tetra- and pentacyclioalkanes from fraction 250-350°C with > 90% content. Chromatograms obtained as a result of gas-chromatographic analysis of concentrates on capillary columns indicate the complexity of their composition, representing a continuous naphthenic background. To simplify composition the polycycloalkanes were subjected to extraction with thiocarbamide. According to the mass spectral data tri-, tetra- and pentacyclioalkanes of the thermo-diffusion fractions have adamantane nucleus in molecule. As a result of studies of polycyclic alkanes and their thiocarbamide extracts using method of GC-MS more than 80 polycyclic alkanes (C_{10}-C_{16}) were detected. Among them the following hydrocarbons were identified: adamantane and a wide range of its homologues (C_{10}-C_{14}), a series of proto-adamantane hydrocarbons, tricyclic undecanes and tricyclic dodecanes (C_{11}-C_{13}); tricyclo [7.3.1.$0^{5.13}$] tridecane - perhydrophenalene; 1-(2-methylhexyl)perhydroindane; tetracyclic adamantanoid hydrocarbons (C_{12}-C_{16}); diamantane ($C_{14}H_{20}$) and its three homologues ($C_{15}H_{22}$). In concentrate of polycyclic alcanes were identified also relict hydrocarbons: isoprenoids (C_{11}-C_{22}), and polymethyl-substituted decalines (C_{13}-C_{21}). The following polycycloalkane hydrocarbons were determined in oil for the first time: 1-n- and 2-n-propyladamantanes, 1-methyl-3-propyladamantane, 1-ethyl-2-methyladamantane, 2-n-butyladamantane, methyltetracyclo [6.3.1.$1^{6,10}0^{2,6}$] tridecane ($C_{14}H_{23}$), 1- and 3-methyldiamantanes, etc. Application of CG-MS method with the system of MS data analysis - AMDIS (Automated Mass Spectral Deconvolution and Identification System) made it possible to obtain the most complete information on the nature of the hydrocarbon composition of difficult to study middle fractions of petroleum, which can be useful both theoretically and for its rational utilization.

O-PETRO 3

THE SIGNIFICANCE OF GC-MS/MS IN OIL-SOURCE ROCK CORRELATION

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Application of gas chromatography-mass spectrometry (GC-MS) and more recently gas chromatography-mass spectrometry/mass spectrometry (GC-MS/MS) represents the unique method for investigations of crude oils and their correlation with source rocks. GC-MS and GC-MS/MS of crude oils and extracts of source rocks, oil shales and coals provide identification and quantification of numerous individual compounds. Among them, biological markers (biomarkers) are of the greatest importance. Biomarker molecules are used for evaluating the source organisms, the reconstruction of depositional environment and the maturity assessment. Biomarkers also can provide information of source rock mineralogy (lithology) and age. Steroids and terpenoids are the most useful biomarkers for correlation purposes. Most of them can be routinely identified by GC-MS, however for identification of the most specific compounds GC-MS/MS is required.

The distribution of C_{27}-C_{29} regular steranes (*m/z* 217) is widely used for assessment of the source of organic matter (OM). However, this approach has limitations, because certain marine algae produce sterols with 27 to 29 carbon atoms. C_{30} steranes (4-desmethyl-24-*n*-propylcholestanes) are much more useful as source indicators, since they are highly specific for marine OM input [1]. However, identification of these biomarkers usually requires application of GC-MS/MS (transition 414 → 217). Apart from steranes, diasteranes, geoisomers having, 13β(H)17α(H), or 13α(H)17β(H) configuration are usually present in the crude oils. High diasterane/sterane ratio is typical of petroleum derived from clay-rich source rocks. Diasteranes are usually abundant in acidic, suboxic to oxic depositional environments. Finally, high diasterane/sterane ratio can result also from high thermal maturity or heavy biodegradation. In the routine GC-MS several diasterane isomers co-elute with sterane isomers which makes accurate quantification of these biomarkers impossible. GC-MS/MS (M^+ → 217) separating the compounds according to number of C-atoms allows precise identification and quantification all of sterane and diasterane isomers.

Gammacerane is pentacyclic triterpenoid which is specific for a stratified water column in marine and non-marine depositional environments, commonly resulting from hypersalinity at depth [2]. Care must be taken to accurately quantify gammacerane using the GC-MS (*m/z* 191). Because of its high degree of symmetry, two identical *m/z* 191 fragments are generated in the mass spectrometer from gammacerane. Thus, a sizable peak on the *m/z* 191 mass

chromatogram represents a low concentration of gammacerane compared with other terpanes. Therefore, GC-MS/MS, 412 → 191 transition is recommended for precise identification of gammacerane.

C_{30} tetracyclic polyprenoids (TPP) are most prominently observed in samples derived from low salinity, i.e. fresh to brackish lacustrine environments, and are generally present in low levels in samples derived from saline, i.e., marine and saline lacustrine, environments [3]. The ratio of C_{30} tetracyclic polyprenoids to sum of C_{26} 27-norcholestanes (which are low in lacustrine and prominent in marine samples) is used to distinguish lacustrine and marine settings. However for identification of both, C_{30} tetracyclic polyprenoids and C_{26} 27-norcholestanes, GC-MS/MS (414 → 259 and 358 → 217, respectively) is required.

Application of GC-MS/MS (454 → 191 and 468 → 191) allowed the identification of series of C_{33} and C_{34} isohopanes (31-methylbishomohopanes, 31-methyltrishomohopanes and 32-methyltrishomohopanes). The ratio of isohopanes to hopanes is useful for distinguishing marine, lacustrine and oils from coaly sources [4].

Series of "early eluting hopanes" (M^+ → 191), as well as C(14a)-homo-26-nor-17α(H)-hopanes (HHs, C-ring with 7 carbons instead of the usual 6; M^+ → 369) have been identified by GC-MS/MS. The C_{30} HH/C_{30} 17α(H)21β(H)-hopane ratio has proved applicable to a wide range of maturation, whereas the ratio of C_{30} "early eluting hopane" to C_{30} 17α(H)21β(H)-hopane is useful to distinguish moderately mature and highly mature OM [5].

In difference to numerous source and maturity related geochemical parameters, parameters related to age of OM are scarce. The most useful age parameters, 24-nordiacholestane ratio (NDR) and 24-norcholestane ratio (NCR) [6] are based on distribution and abundance of C_{26} steranes. Identification and quantification of these biomarkers requires GC-MS/MS (358 → 217).

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O-PETRO 4

ROCK-EVAL PYROLYSIS AND PYRO-GCXGC-MS FOR STUDY OF ORGANIC MATTER FROM THE BAZHENOV FORMATION

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The Bazhenov Formation (BF) is one of the largest oil shale formations on the Earth located in Western Siberia, Russia. BF has complex mineral composition (clay-carbonate-siliceous) with high content of organic matter (OM) (5-20 wt. %) in a form of hydrocarbon gases, oil, bitumen and kerogen. The objective of the research project was the detail study of organic matter from BF using standard methods of Rock-Eval pyrolysis [1] and modern approach based on Pyro-GCxGC-TOFMS [2]. Samples of BF rock and oil from different regions of Western Siberia, characterized by different level of OM maturity were studied. Standard Rock-Eval analysis of rock and kerogen has been done by HAWK resource workstation (Wildcat Technology, USA). Advanced study of organic matter, including rocks, kerogen, oil and extracts have been executed using Pyro-GCxGC-MS Pegasus 4D (LECO Corporation).

Data on total organic content, oil saturation, kerogen type, kerogen maturity, generation potential of the rock, chemical composition of pyrolysis products in temperature range from 300 to 650^{o}C and kinetics of kerogen thermal decomposition were determined for rock samples. Detailed chemical composition, including group content of hydrocarbons (aliphatics, aromatics, heteroatom compounds, *etc.*) and biomarker ratios have been calculated for samples of oil and organic extracts from rock samples [3].

Results of the study provided an opportunity to make a conclusion on the genesis of OM and conditions of OM transformation in geological history at the stages of sedimentation, diagenesis and katagenesis for several different regions of Western Siberia. Data on kinetics of immature kerogen thermal decomposition were applied as input data for petroleum basin modeling. Obtained results were also used for evaluation of potential of thermal EOR (steam injection, *in situ* combustion) for hydrocarbon production of the Bazhenov Formation.

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O-PETRO 5

STUDYING KINETICS OF ARTIFICIAL AGING OF BALLPOINT PEN INK STROKES USING LIQUID CHROMATOGRAPHY MASS-SPECTROMETRY

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One of the central problem of the documents forensic investigation is the setting the time and sequence of production of document details including chronological sequence of intersecting strokes and time interval and sequence of execution of document copies.

As a rule, the writing down of signatures or any handwritten notes are carried out by ballpoint pens with blue color inks, in connection with it, researches are mainly focused on the study of this type of pen inks. However, different modern physical and chemical methods do not always solve the problem of interpreting the obtained results due to the complexity of the analyzed objects, as well as the influence of external parameters on degradation processes

To solve the problem of determination of records aging made by ballpoint pens, it is necessary to get information about the composition of ballpoint pen inks, and about qualitative and quantitative changes of some components that may occur during aging. Moreover, it is necessary to know the laws of the features formation due to the paste production process, temporary changes in the composition and properties of paste from the moment of applying the stroke, changes in the composition and properties of paste caused by environmental influences or caused by intentional effects on document such as photo-, thermo-, UV-, IR-, microwave and other types of external influences.

The study of artificial aging processes of dyes in the ink strokes of ballpoint pens *BIC Original, Corvina 51* and *Pilot BPS* exposed to the thermal effect was carried out. As the exposure time of the thermal effect increased, a visible change of degradation products content relative to the initial dye was observed. The kinetic characteristics of dyes degradation processes have been revealed, which make it possible to predict the characteristic correlations of the dyes and their degradation products content.

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O-FOOD 1

IN SOURCE DERIVATIZATION OF ALCOHOLS FOR FAST PROFILING OF STEROLES IN FOOD BY DART-MS

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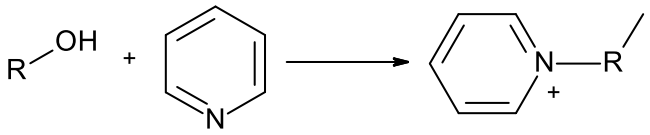
Fast growing popularity of ambient ionization mass spectrometry methods is caused by the ability of these techniques to provide express qualitative and, sometimes, quantitative analysis without or with minimal sample preparation. At the same time, all of these approaches inherited mainly such 'soft' ionization processes as protonation, cationization and deprotonation. Thus, analytes, which are not capable of these processes, have high detection limits or cannot be analyzed by such methods at all. Furthermore, some compounds readily eliminate leaving groups after ionization. Some of these problems can be overcome by using the chemical modification approaches providing the permanent charge derivatization or yielding readily ionizable derivatives. The main requirement for probable derivatization methods involved in analysis by ambient ionization mass spectrometry is the application of extremely simple and fast reaction procedures. Herein, we describe the first example of such approach for analysis of alcohols by 'direct analysis in real time' (DART) mass spectrometry. The proposed method is based on reaction of alcohols with pyridine directly in DART sample gap yielding fixed-charge derivatives:



The approach was tested on linear and branched fat alcohols, cyclic alcohols and sterols. It was shown, that the process takes place only under rather high temperatures of helium flow and suitable only for high boiling alcohols. The recorded DART mass spectra display only the peaks for cationic part of the derivatives. The latter demonstrate high ionization efficiencies and their limits of detection decrease by two orders of magnitude. The described method was also used for the detection of sterols in complex food matrices. This opens the possibility of its application for profiling of such compounds in food samples.

The publication was prepared with the support of the "RUDN University Program 5-100"

O-FOOD 2

NEONICOTINOID PESTICIDES IN SLOVENIAN HONEY AS DETERMINED BY LC-MS/MS AND TWO DIFFERENT SAMPLE PREPARATION TECHNIQUES

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Neonicotinoid pesticides were considered, up until recently, a major advancement in the field of pesticides given their effectiveness and low toxicity towards non-target species, as well as their degradability in the environment. This claim is seriously reconsidered due to an apparent link between neonicotinoids and colony collapse disorder in bees. In 2011, Slovenia has imposed a moratorium on certain neonicotinoids but there has been no country-wide study looking at the effectiveness of the ban or indeed levels of those neonicotinoid pesticides still regulated. Using honey is a non-invasive way of checking for the residues of registered and nonregistered neonicotinoid pesticides to which the bees could be exposed.

We developed an effective LC-MS/MS method combined with a suitable sample preparation method for the analysis of trace residues of neonicotinoid pesticides in honey. Two sample preparation methods (solid phase extraction – SPE and QuEChERS) were chosen. Honey is a difficult matrix to analyse, which accounts for the relatively few published studies. Both QuEChERS and SPE have been used individually in a few studies but no one, until our study, has so far looked at which method, according to the agreed parameters, is the best for honey preparation prior to analysis. In our study, both extraction methods were optimized, fully validated, and compared in terms of validation parameters and their compatibility with LCMS/MS. Furthermore, calculation of uncertainty of determination according to SANTE/11945/2015 protocol was made for each of them. Validation was performed at two levels (10 μg/kg and 50 μg/kg). Both methods gave satisfactory recoveries (68.2–113.6%), precision (0.9–8.0%), low limits of detection (0.05 to 0.97 μg/kg), and quantification (0.19 to 3.25 μg/kg). Expanded uncertainty (k = 2, confidence level 95%) using SPE was 17.8–50.1% (10 μg/kg) and 5.2–16.3% (50 μg/kg), and 10.0–30.1% (10 μg/kg) and 5.3–10.1% (50 μg/kg) for QuEChERS. Therefore, both extraction methods gave satisfactory validation parameters and low combined uncertainty of determination, but the method using QuEChERS showed slightly better accuracy and lower matrix effect than SPE. It was therefore chosen for further work and applied to the analysis of 51 honey samples collected from across Slovenia in the period 2014-2016. These were obtained from the Slovene Beekeeping Society data bank and were representative for the whole of Slovenia (Figure 1).

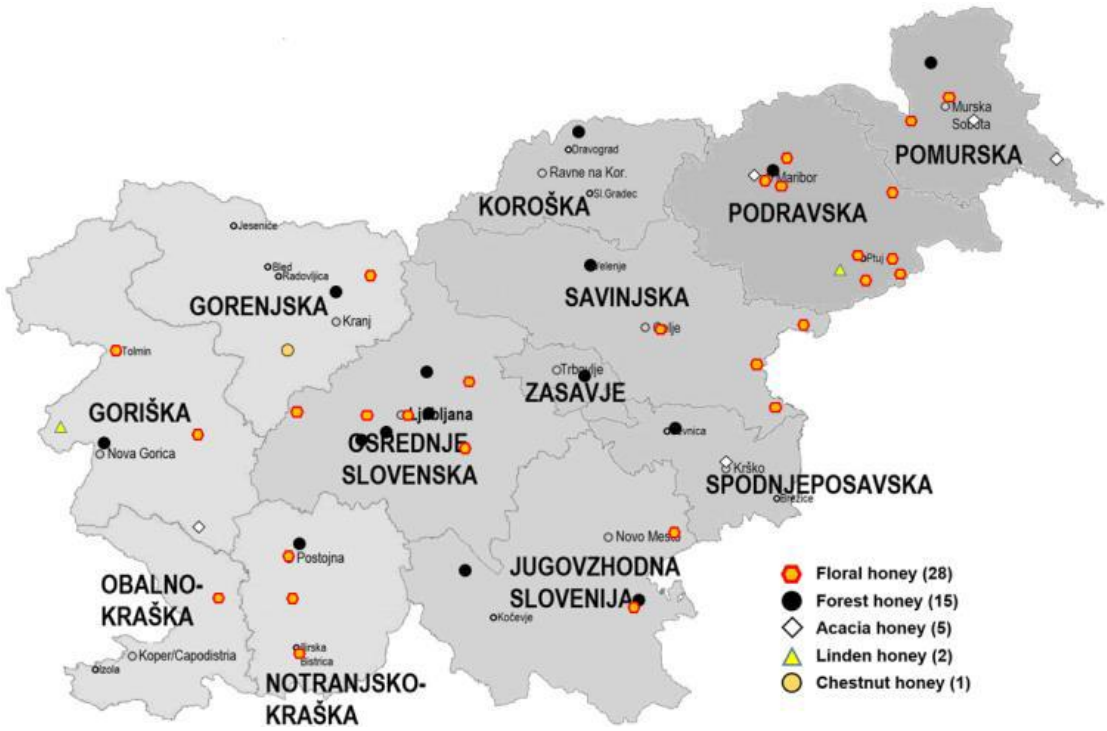

Figure 1: The origin of different honey samples shown on the map of Slovenia.

The results showed low contamination of Slovenian honey with target neonicotinoids (below MRLs), but not their complete absence. In spite of time gap between the implementation of the current ban in 2011 and the collection period of our samples (2014-2016), neonicotinoids are still present in the honey, indicating that the current ban is not fully effective and that there are still some unidentified sources of contamination. Slovenia has a long history of bee-keeping and is the origin of one of widespread honeybee subspecies (Carniolan honeybee; Apis mellifera carnica, Pollmann). Therefore, this survey of Slovenian honey is an important contribution to the worldwide database of neonicotinoid contamination and the threat it poses to the honeybees.

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O-FOOD 3

ANALYSIS OF CANNABINOIDS BY LIQUID CHROMATOGRAPHY TANDEM MASS SPECTROMETRY OPERATED IN POSITIVE ELECTROSPRAY IONIZATION MODE

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Cannabis sativa L. is a multy-use crop known for a wide range of bioactivities. The spectrum of *Cannabis* phytochemicals is extremely complex, up to now, almost 600 secondary metabolites have been indentified and among them more than 200 endogenus cannabinoids. Over the past two-three years, the popularity of *Cannabis* plants and cannabis-based products has significantly increased, as many countries around the world have adopted a more liberal view towards the use of this plant for medicinal purposes. Cannabidiol (CBD) and delta-9-tetrahydrocannabinol (THC), indentified as the primary active component, due to their biological activities are the compounds which drown significant attention in *Cannabis* plants. The reliable analytical method for the determination of cannabinoid potency in *Cannabis sativa* plants and *Cannabis* infused foods (dietetic supplements) was developed. The extraction of cannabinoid was included in 1 gram homogenized food (100 mg plant) sample, hydrated with 10 mL of reagent water for 30 min. After that time 10 mL of acetonitrile was added followed by the addition of EN15662 QuEChERS extraction salts for the analyte partitioning and phase separation. After the centrifugation the supernatant was either diluted (for canabinoides in plant samples) or underwent a secondary dSPE cleanup before the analysis. The linearity was checked for the range from 0.05 to 1.0 μg/mL for THC. The limit of quantification was 0.002% for plants and 0.5 mg/kg for supplements, the accuracy comparing two chromatographic techniques (LC-MS/MS and HPLC-DAD). In the five *Cannabis sativa* samples the presence of HCH was analyzed. The level of THC did not exceed the value established by the national Regulation (Off. gazz. RS 64/2013) and Comm. Reg. EC 1420/98 (the weight of THC in the weight of a sample maintained at constant weight is no more than 0.2% for the purposes of the grant of aid for marketing). In three dietetic supplement samples the detections of THC were in accordance with the Off. gazz. RS 45/2010.

O-FOOD 4

INVESTIGATION OF EXTRACTED AND LEACHED ANALYTES FROM PACKAGING MATERIALS WITH GC-TOF MS

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Migration of analytes from packaging material into food products is a concern for manufacturers and consumers because of the potential to contaminate food and beverages. The extraction and/or leaching can impact the quality of the product, the integrity of the packaging material, and cause concern related to consumer health and product safety. A general extraction of a variety of food packaging products, including sealable plastic bags and plastic food containers, was performed. Solvent was placed inside each packaging product for an extended period of time and then concentrated through evaporation prior to analysis. General screening of this extract with non-targeted analytical techniques was used to understand what analytes were present and may have the potential to migrate into the food. GC was used for separating analytes from each other and TOFMS provided full mass range data. Nominal mass TOFMS data were acquired and were searched against library databases for tentative identifications. High resolution TOFMS data were also acquired to add confidence to identifications with accurate mass information. Several analytes were determined in the various packaging types and are highlighted here.

O-FOOD 5

MACHINE LEARNING EFFORTS AT NIST FOR EXTRACTING INFORMATION FROM CHEMICAL DATA SETS

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Given the diversity of complex chemical reactions, combined with the fact that these nondynamical processes are multivariate in nature, makes it very challenging to fully characterize them. From the scientist's perspective, the main challenge entails the use of highly accurate and reliable measurements (most of the time involving different instrumentation) from which the essential characteristics (i.e. variables, parameters, etc.) of complex chemical systems necessary to reproduce their behavior can be assessed. Furthermore, an additional and important challenge is related to the development of appropriate data science and informatics tools to distill this experimental information into reliable models that could aid in the development of novel chemical manufacturing processes or the modification of some of these processes in an in-operando manner, improving the versatility of manufacturing while reducing cost. Given that connecting chemistry to functionality requires the ability to perform spatially and temporally resolved chemical analysis across length and time scales, this task remains a grand challenge for researchers in government, academia and industry.

In response to these growing needs that require new and effective approaches in computational science, data management, statistics and machine learning (ML), the Chemical Sciences Division at NIST has started dedicating efforts focused on generating critical mass in the development, implementation and validation of a wide variety of ML tools that can help address these needs. In the Chemical Sciences, ML tools have been very helpful in the "mining" of information from large data sets with a high degree of complexity in areas such as chemical kinetics & reactivity, high resolution spectroscopy, rational design of materials, integrated omics, catalysis, monitoring and control of chemical processes, and forensics, to name a few. Recently, the scientific world has been taken over by a revolution in the area of machine learning (ML). In essence, ML is a field of computer science that allows computer systems to extract patterns from data ("learn from data") in an automated fashion without the need for explicit programing or guidance from an expert. Everyday scientists and the community at large witness the use of ML to analyze complicated and massive amounts of data leading to major advances in a wide range of scientific and technological applications.

In this talk, a brief description of the Chemical Sciences Division's plans to establish a program in machine learning for extracting scientific information from chemical data sets will be provided. In addition, some examples illustrating applications and results of these efforts will be discussed, followed by an outlook of our future plans.

O-ENV 1

CHROMATO-MASS-SPECTROMETRIC STUDY OF TOXIC PRODUCTS OF ROCKET FUEL TRANSFORMATION

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Presented combination of different chromate-mass-spectrometry methods (CMS), first GS-MS, LS-MS and TLC-MS for completive determination and identification of toxic products of rocket fuel transformation. Hydrocarbon and hydrazine propellants transformation products discussed. The primary attention is devoted to the development of physicochemical grounds of the use of various CMS procedures to solve topical problems in this field.

The investigation of rocket fuels (unlike jet fuels) is often subject to special requirements: it is necessary to determine not only impurities and trace components but also the isomeric composition of the components. Isomers, which often have similar mass-spectra and retention characteristics, can be identified by combination of molecular-statistical, mass-spectrometric and chromatographic methods. Such approach well developed for gas-adsorption chromatography – mass-spectrometry.

LC – MS methods developed for determination and identification of 1,1-dimethylhydrazine and it transformation products in complex mixtures with hydrocarbon fuels. Methods based on HPLC on Hypercarb sorbent, semi-empirical molecular-statistical calculations and MS with electrospray/atmospheric pressure chemical ionization.

Surface-assisted laser desorption/ionization mass-spectrometry (SALDI) was applied to study the products of 1,1-dimethylhydrazine and rocket kerosene transformation on the surface of construction materials. Some time it is possible to use real metal sample as thin-layer chromatography plate. The approach proposed make it possible to distinguish the transformation products of 1,1-dimethylhydrazine and rocket kerosene from the low-molecular-weight compounds and oligomers utilized in the production of construction materials, with undergo different transformation in the course of operational processes.

The application of CMS for the development and evaluation of processes for determination for decontamination of equipment, industrial wastes and soils from rocket fuel components is substantiated.

O-ENV 2

SAMPLE STACKING AND ON-LINE DERIVATIZATION FOR THE ANALYSIS OF AMPICILLIN AND AMOXICILLIN BY MICROEMULSION ELECTROKINETIC CHROMATOGRAPHY

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Microemulsion electrokinetic chromatography (MEEKC) is an electrodriven separation technique which uses microemulsion buffer as a background electrolyte. In recent years MEEKC has gained considerable attention and widespread application because of its usefulness for determining the substances, which are different in their electrophoretic mobilities, and offers the possibility of highly efficient separation of both charged and neutral solutes covering a wide range of water solubilities.

Microemulsion can be used as a reaction medium for providing many chemical reactions due to its unique composition. In our work it was shown that derivatization of ampicillin (AMP) and amoxicillin (AMO) with naphthalene-2,3-dicarboxaldehyde (NDA) is accelerated greatly in microemulsion, compared with the standard derivatization procedure, no heating being required. This permits the reaction to proceed in the capillary in on-line mode. A novel method using MEEKC combining the concentration technique called reversed electrode polarity stacking mode (REPSM) with subsequent on-line derivatization was developed for the quantitative determination of antibiotics. The effect of each individual component within the microemulsions, i.e. the oil phase, the surfactant, the co-surfactant and the buffer concentration on the resolution of the analytes was systematically studied.

The limits of the detection were 150 μg/l for AMO and 110 μg/l for AMP. The method developed allowed us to decrease the detection limits by about 200-fold, to reduce the analysis and preparation time considerably, to diminish the consumption of the expensive reagents and to avoid high temperatures during the derivatization procedure.

O-ENV 3

GC-MS STUDY OF CATALYTIC CONVERSION OF TERPENE ALCOHOLS ON MICRO-MESOPOROUS ZEOLITES

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Geraniol (3,7-dimethyl-trans-2,6-octadiene-1-ol) and its cis-isomer nerol are valuable aromatic substances having subtle perfume of rose aroma and used in perfumery, also they are strategic raw materials – "building units" in syntheses of A, E and K vitamins, carotenoids, ionones and methyl-ionones. Commercial production of geraniol and nerol (up to 10 thousand tons annually) generally is based on the catalytic liquid-phase isomerization of linalool (3,7-dimethyl-1,6-octadiene-3-ol). Catalytic transformation of terpene alcohols include not only isomerization, but also their dehydratation, cyclization and condensation. These processes have been studied by us earlier for linalool [1], this report presents data on catalytic transformations of geraniol.

The same micro-mesoporous catalysts synthesized by recrystallization of commercial BEA- zeolites in NaOH aqueous solutions and characterized by chemical composition, pore volumes and specific surface areas defined by nitrogen adsorption-desorption, and the acid properties estimated using temperature-programmed desorption of ammonia, have been used in experiments carried out in an atmosphere of nitrogen or argon in a liquid phase at 27–150°C. The analysis of products of catalytic transformations was carried out by the GC-MS (Agilent Technologies, 5890B/5977A, capillary column HP-5ms, Ultra Inert, 30 m x 0.32 mm x 0.25 μm); the main products are β-linalool, trans-geraniol, trans,trans-farnesol and (2E,6E)-6,11-dimethyl-2,6,10-dodecatrien-1-ol, small quantities of β-mircene, D-limonene, trans-β-ocymene, β-ocymene, α-terpineol, nerol, cis-isogeraniol, trans,trans,trans-geranylgeraniol, p-camphorene and unidentified isomer of trans-geranylgeraniol are present.

It is established, that in "zeolitic reactor" it is possible to receive such large molecules as trans,trans-farnesol and (2E,6E)-6,11-dimethyl-2,6,10-dodecatrien-1-ol at a relatively low temperature, by one-pot method and with selectivity up to 35 and 52%, respectively.

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O-ENV 4

NOVEL DISINDECTION BY-PRODUCTS IN THE ARKHANGELSK DRINKING WATER

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Drinking water chlorination has been actively used since the beginning of the XX century. Although chlorination helps destroying pathogenic microorganisms it leads to the formation of a wide range of toxic disinfection by-products (DBPs). The latter appear due to reaction of active chlorine species with various compounds dissolved in water including both natural and anthropogenic. Although the list of the known DBP, contains now more than 700 compounds, it is far from being completed, while only 50% of the total organic halogens in drinking water belong to the known compounds.

Water samples were collected in March 2017 in the period of active snow melting, and after the high water period in June 2017. That set included a sample from the Severnaya Dvina river at the water intake of Arkhangelsk, a sample after mechanical purification and coagulation, and a sample after chlorination. To extract and concentrate organic compounds SPE Bond Elute PPL cartridges (Agilent, Folsom, USA) with modified polymer styrene-divinylbenzene sorbent were used. Two liters of water acidified to pH 3 by formic acid were made pass at 5mL/min using vacuum manifold through SPE cartridges. High resolution QTOF mass spectrometer TripleTOF 5600, (AB Sciex, Canada) with ion source Duospray connected to the HPLC system LC-30 Nexera (Shimadzu, Kyoto, Japan) was used.

Non targeted screening of the organic compounds in the Arkhangelsk tap water with HPLC-ESI (APCI)-QTOF HRMS allowed detecting over 350 compounds including 50 halogenated ones. Accurate mass measurements provided elemental composition of all these products. A group of 4 compounds had elemental composition C6HnX6-nO (X = Cl, Br). Fragmentation pattern demonstrated these compounds to be trichloro-, dichlorobromo-, chlorodibromo and pentachlorophenols.

The elemental compositions of the largest group were (CnH2nNO2X, CnH2n+2NO2X and CnH2n+1NOX2 (X = Cl, Br). MS/MS allowed referring them to halohydrines or dihalogenated fatty amides, the products of conjugated electrophilic addition of halogens to the double bonds of unsaturated fatty amides. The proposed structures were confirmed by conducting aqueous chlorination with standard solution of oleamide. These compounds may be considered as a brand new class of disinfection by products, while their toxicities require special study.

Five detected species belong to halogenated aromatic carbonyl containing compounds. Three of them lose CO2 molecule in CID, as deprotonated acids. 3,5-dichloro-4-hydroxybenzoic acid was already reported as DBP, while two others were identified as dimethylbromobenzoic and dimethyldibromobenzoic acids. Two others were new and tentatively identified as trichlorophenylacetate and 2,4-trichloro-1,3,5-benzotrialdehyde. Four compounds of the fourth group contained nitrogen? and were better represented by positive ion spectra. Thorough manual work with the spectra and ChemSpider data allowed proposing 3,4-dichloro-2-methoxy-5-oxo-2,5-dihydro-1H-pyrrol-1-yl)-acetic acid for one of them (library score 90%). The others were tentatively identified as substituted halo pyridines.

O-ENV 5

OCCURENCE OF SELECTED PHARMACEUTICAL COUMPOUNDS AND THEIR METABOLITES IN MEDITERRANEAN COASTAL ENVIRONMENT

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The occurrence of pharmaceuticals has been widely described in fresh surface and ground waters [1], but less investigated in the marine environment, although it represents the last receiver of the continental contaminations. Moreover, many municipalities discharge treated wastewater into marine coastal waters, and little is known on the environmental impact of such practices. In Europe, the Marine Strategy Framework Directive [2] placed pharmaceuticals on the indicative list of elements covering the qualitative and quantitative mix of pressures on the environmental status of marine waters. Thus, pharmaceuticals monitoring data in marine waters are necessary to assess the water quality and enhance future regulations and management decisions [3]. The presence of pharmaceuticals metabolites is less investigated, also it has been shown that they can remain as ecotoxic as the parent compound or more dangerous.

The development of analytical methods for the analysis selected pharmaceuticals and their metabolites in marine sediments is reported here.
Freeze-dried sediment samples were extracted using accelerated solvent extraction, then purified using solid phase extraction the overall extraction yield was above 80% for all target compounds and matrix effects were evaluated and minimised. The consecutive analysis was performed using using LC-QToF-MS. An optimisation of mass spectrometric parameters was assessed in order to achieve low quantification limits (around 1pg injected).

This method has been successfully applied for monitoring campaigns in 2 Mediterranean sampling sites impacted by wastewater effluents from Marseille and Montpellier (France). Triplicate analysis of 30 samples showed concentration ranging from 1 (O-desmethyl metoprolol) to 6000 $ng.kg^{-1}$ (azithromycine).

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O-ENV 6

ORGANIC POLLUTANTS IN THE SNOW OF RUSSIAN ARCTIC ISLANDS: 2016-2017 EXPEDITIONS

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Arctic environment previously has been shown to be very sensitive to changes in the chemical composition of the air–snow interface and climate changing in general. Snow has been used as an efficient indicator of air pollution in cold climate regions due to "cold finger" effect. Regular monitoring of the Arctic environment can give insight in the understanding of the global air transfer processes and identify pollution sources. This study represents results obtained during research program of Northern (Arctic) Federal University "Arctic Floating University". Snow samples were taken within the expeditions to Novaya Zemlya Archipelago carried out by "Prof. Molchanov" ship in 2016 and 2017. The sample preparation procedure involved melting of the snow samples under room temperature and further extraction with dichloromethane according to US EPA 8270 method. The extracts were analysed using Pegasus GC-HRT instrument (LECO, USA). Hydrocarbons (alkanes, napthenes and PAH), phthalates, fatty acids and some natural organic compounds (terpenes and terpenoids) were the main organic constituents of the samples. Only several US EPA priority pollutants were identified and quantified (phenol, pyridine, phthalates, some PAH). Large number of identified fatty acids signifies the intensive photo-oxidation processes in the atmosphere or on the snow surface involving hydrocarbons. Unexpectedly high levels of oxygenated alkanes with DBE=0 were established in all the samples. Considering the previously obtained, these compounds could occur as a result of photo-oxidation processes involving saturated hydrocarbons. One more interesting class of compounds which is worth mentioning corresponds to fatty amides. Their origin may involve humic matter or some anthropogenic sources. On the contrary persistent organic pollutants (POP), which are usually used as environmental indicators, were poorly represented only by several phosphates (for example tri(2-chloroethyl) phosphate).

The research was done in terms of RSF 17-13-01112 project.

O-ENV 7

DETERMINATION OF COTININE AND 5-HYDROXYINDOLE-3-ACETIC ACID AS POPULATION MARKERS IN WASTEWATER BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY COUPLED WITH TANDEM MASS-SPECTROMETRIC DETECTION

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Analysis of biomarkers in wastewater is increasingly seen as an important tool for valuation of health, nutrition and use of various substances by humans. Some biomarkers are used for population estimates, since the actual values of population size in cities can differ significantly from official counts, which inevitably leads to errors in assessing the impact of various factors to people calculated per capita. Cotinine and 5-hydroxyindole-3-acetic acid (5-HIAA) are the main metabolites of nicotine and serotonin, respectively, which are excreted by urine and can be used as biomarkers for population estimates.

The determination of these metabolites is more preferred than the detection of nicotine and serotonin themselves in terms of correctness of the results. There are numerous methods for the determination of cotinine and 5-HIAA in urine by HPLC-MS/MS. However, there are only few works in the literature devoted to the determination of these compounds in wastewater with detection limits up to 1 μg/L. Considering such low and varied concentrations of cotinine and 5-HIAA in wastewater, it is vital to develop a reliable and highly sensitive procedure for the determination of these compounds.

A technique of liquid-liquid extraction and subsequent quantitative determination of cotinine and 5-HIAA in wastewater by high-performance liquid chromatography in combination with tandem mass spectrometric detection was developed. Poroshell Hilic column was used as a stationary phase which has an alternative selectivity compared to traditional C18 columns. Developed procedure is characterized by low detection limits (0.1 μg/L for cotinine, 0.2 μg/L for 5-HIAA) and good selectivity. This technique provides reliable assessment of the concentration of cotinine and 5-HIAA in wastewater of Moscow region.

The work was carried out with financial support of the RFBR grant 16-03-00257.

O-ENV 8

MODULATION AND RESILIENCE OF THE METABOLOME OF *PSEUDOMONAS GRAMINIS*, A CLOUD BACTERIUM, FACING H_2O_2 ATMOSPHERIC STRESS.

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In cloud waters microorganisms are metabolically active although they are exposed to very strong stresses, especially due to the presence of reactive oxygenated species, including H_2O_2 and radicals. In order to understand how microorganisms can modulate their metabolism facing H_2O_2 stress, we have investigated by a metabolomics approach the response of a *Pseudomonas graminis* strain, isolated from cloud waters, to hydrogen peroxide exposure. For this purpose *P. graminis* cells were incubated in microcosms containing artificial cloud waters in the presence or absence of H_2O_2. Metabolites were extracted at two time points (50 min and 24 h) that were important regarding the evolution of ATP cellular content and H_2O_2 degradation over time. These bacterial extracts were analysed by LC-MS and ^{1}H-NMR using the Metabolic Profiler® facility (Bruker). Metabolic profiles were converted into matrices and statistical analyses (PCA, PLS-DA) were performed; key markers of this oxidative stress were identified by 2D NMR and LC-MS-Orbitrap. At time 50 min, when H_2O_2 was still present in the incubations, the bacteria adapted and modulated their metabolome facing this stress. The major metabolic pathways of *Pseudomonas graminis* (13b-3) impacted by the presence of hydrogen peroxide were the carbohydrate pathway, glutathione, energy, lipid and amino-acid metabolisms. Unexpectedly, the concentration of a few dipeptides containing mainly Ala, Val, Leu (Ile) was also highly modified in the presence of H_2O_2. These dipeptides are reported here for the first time as biomarkers of oxidative stress. Interestingly, at time 24 h, no more significant difference was observed between the metabolites of exposed and non-exposed cells to H_2O_2, showing the resilience of this bacterium metabolome after H_2O_2 stress exposure.

O-ENV 9

DETERMINATION OF α-PINENE OXIDATION PRODUCTS WITH GC-MS AND LC-MS/MS

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Terpenes are a large and diverse class of organic compounds, produced particularly by conifers, which represent nearly half of all volatile compounds emitted in the atmosphere. They oxidize in successive reactions in the atmosphere, forming less volatile products, called secondary organic aerosols (SOA). Atmospheric aerosols can influence the climate and are damaging to health, causing acute and chronic diseases. Due to anthropogenic activities, the concentrations of the aerosols are increasing. The second most abundant terpene, after isoprene, is α-pinene, whose emissions are increasing.

SOA quantities in the air are underestimated by the current atmospheric models which suggests missing or neglected reaction mechanisms. For example, the singlet oxygen is not yet included in the global atmospheric models and may be one of the atmospheric oxidants, which could fill the gap between the modelled and the measured SOA. *α*-pinene was used as a model compound for studying singlet oxygen importance in SOA production.

Preliminary experiments were done in acetonitrile with photochemically generated singlet oxygen. The oxidation products were determined with LC-UV detection, which showed only one major oxidation product. Further chromatographic analysis coupled to MS, such as high resolution tandem MS, IT-TOF with APCI ionization, were performed. Results of LC-MS analysis pointed to pinocarvone as the major oxidation product, which was also supported by GC-MS analysis. Additionally, some other common oxidation products were identified, such as: *cis*-pinene-3-ol, pinocarveol and myrtenal. Quantitation and determination of kinetic rates of these oxidation products will be our next step. Study suggests that singlet oxygen can play a significant role in atmospheric oxidation processes and can be the missing part of current SOA chemistry.

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O-ENV 10

GC-MS SCREENING OF SEMI VOLATILE ORGANIC POLLUTANTS IN MOSCOW RAIN

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Rain and snow analysis are often used to estimate atmospheric pollution. For several years we were studying Moscow (Russia) air pollution during the winter period by analyzing the snow samples collected at the end of the winter season. To estimate the atmospheric pollution in a warm season eight samples of rain were collected in two districts in Moscow from April-May 2017. As we did not know what to expect in those samples the non-targeted analysis was performed using one- and two-dimensional gas chromatography coupled to a novel, extremely sensitive TOFMS. Besides detecting and quantifying compounds from the list of priority pollutants, enhanced separation and detection capabilities of the method allowed identification of novel pollutants from various organic compound classes.

The rain samples were collected to the amount of 250-1000 ml using a wide glass funnel. The samples were prepared for analysis in accordance with USEPA 8270 method. Pegasus® BT GC-TOFMS (LECO Corporation, Saint Joseph, MI, USA) was used for the 1D GC analysis and a novel TOFMS prototype coupled to GCxGC was used for 2D GC data collection. The data were acquired at an acquisition rate of 10 full (10-800 m/z range) spectra per second in 1D runs and 200 full spectra per second in 2D runs. Several types of blanks (laboratory, sample preparation method) were used to exclude false positive results. The quantitation was performed using response factors relative to the isotopically labeled internal standards.

Since sample preparation was carried out immediately after sample collection the loss of semi volatile compounds due to biological or physical-chemical degradation were minimal. More than 500 semi volatile organic compounds were identified in the samples. They were divided into three groups according to their identification reliability. The first group (56 compounds) includes analytes from the USEPA priority pollutants list. All those analytes were also quantified. Polycyclic aromatic hydrocarbons, phenols, phthalates, organochlorines, including PCBs were the most represented classes inside the first group. Detection of various nitrophenols and oxidized PAH at the notable levels suggests the chemical processes are occurring in the clouds.

The second group (over 250 compounds) represents reliably identified chemicals with high NIST library similarity scores, matched retention indices (when available), correct accurate masses of all ions in deconvoluted mass spectrum and correct fragmentation pattern (checked manually). Aldehydes, ketones, alkanes, fatty acids, aromatic hydrocarbons and their numerous

derivatives, halogen containing compounds, furans, amides, organophosphates, glycols, N- and O-containing heterocycles, including pyridines, quinolines, indols and others were the constituents of this group.

The third group of the detected analytes consisted of the partially identified chemicals, when only elemental composition, affiliation to a certain class based on chemical space in the 2D GC plot, or the presence of certain functional groups as indicated in mass spectrum was established. Multiple examples are discussed where using GCxGC-TOFMS data was especially critical in structural elucidation of the challenging cases.

The obtained results were very useful for comprehensive estimation of the environmental pollution of the Moscow air and for selection the candidates for including in the city's priority pollutants list.

O-ENV 11

APPLICATION OF LIQUID CHROMATOGRAPHY/ELECTROSPRAY IONIZATION TANDEM MASS SPECTROMETRY FOR THE ELUCIDATION OF HYDROXYL RADICAL OXIDATION OF METSULFURON METHYL AND NITROSOMORPHOLINE

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Sulfonylureas are among the most important class of antidiabetic and herbicides. Solar light excitation and Advanced Oxidation Processes may result in the formation of a wide array of products owing to the relative complex structure. These products, that should be identified, may present a more toxic effect than the parent compound.

Liquid chromatography/electrospray ionization quadrupole time-of-flight mass spectrometry (LC/ESI-QTOFMS) with accurate mass determination emerges as a valuable technique for the precise elucidation of all possible byproducts. The hydroxyl radical was generated by excitation of the iron(III) aquacomplex $[Fe(H_2O)_5OH]^{2+}$ and hydrogen peroxide at pH 3.5 - 4. The studied products were Metsulfuron methyl (MTSM) and nitrosomorpholine (NMOR)

Several products owing to the reactivity of hydroxyl radicals with sulfonylurea and nitrosmorpholine were obtained. In the first case, the main products arise from scission of the sulfonylurea bridge, hydroxylation of the aromatic ring, demethylation of the methoxy group and more importantly and unequivocally from the rupture of the triazine skeleton. To reach such scission, a primary demethylation of the methoxy group on the triazine moiety seems to act as a precursor process. Such a process was observed with the three studied sulfonylurea compounds. In the case of nitrosmorpholine, the elimination of the nitroso and the scission of the cycles moieties were clearly identified as the first steps to the mineralisation of the solution.

The reported results demonstrated the usefulness of accurate mass measurements undertaken by LC/ESI-QTOFMS for structural elucidation of the unknown byproducts that were generated during hydroxyl radical reactions with sulfonylureas and nitrosomorpholine. It has been possible herein to identify the structures of products arising from the opening of the recalcitrant triazine structure via hydrolysis processes in acidic solutions.

O-ENV 12

DETERMINATION OF POLAR BENZOTRIAZOLES WITH MICROEXTRACTION METHODS AND LC-MS/MS

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Benzotriazole and its polar derivatives are used for their anti-corrosive properties in different industrial fluids, but also in household dishwasher detergents. Because of their widespread use, polar properties and poor biodegradability, they have been detected in surface water, wastewaters, groundwater and drinking water, in river sediments, soils and house dust in concentration ranges ng/L–µg/L. Their main way of entry into the water cycle are wastewater treatment plants' effluents and they are classified as emerging pollutants due to their harmful effects on plants and toxicity to some aquatic organisms. Since they are expected in low concentrations, their determination demands the use of preconcentration techniques, most commonly solid phase extraction (SPE), combined with sensitive analytical techniques, such as LC-MS/MS.

Solvent microextraction techniques require only microliter amounts of solvents and are therefore regarded as more environmentally friendly than classical extraction techniques. Two of these techniques, dispersive liquid-liquid microextraction (DLLME) and hollow fibre liquid-phase microextraction (HFME), were in this work optimized for the extraction of six polar benzotriazoles from aqueous samples. The extracts were analysed with LC-MS/MS.

For DLLME, a fast injection of a mixture of a water-immiscible extraction solvent and a miscible dispersive solvent into an aqueous sample forms a stable emulsion, which offers a very large interfacial surface and consequently the equilibrium state is reached very quickly (Figure 1). With the aid of a centrifuge, the phases are then separated and the extract collected [1]. For optimal enrichment factors the following parameters were optimized in addition to the selection of the correct extraction and dispersive solvents: sample volume, pH and ionic strength, volumes of solvents chloroform and acetonitrile, centrifugation speed and time. At optimal conditions, the enrichment factors for the analysed benzotriazoles ranged from 10 to 85, according to their polarity.

For HFME, the pores of a hydrophobic hollow fibre are filled with a small amount of an organic solvent, across which analytes diffuse into the acceptor phase placed in the lumen of the fibre (Figure 2). The presence of the membrane increases the interfacial area between sample, which results in high enrichment factors and good clean-up of the matrix components [2]. The optimization of this method included the selection of the membrane solvent and acceptor solution,

and experimental optimization of the sample volume, pH and salt content, fibre length, acceptor solution pH, speed of stirring and extraction time. At optimal conditions, the enrichment factors for the analysed compounds ranged from 38 to 159, again with correlation to their polarity.

Figure 1: Scheme of the DLLME extraction procedure
Figure 2: Scheme of the HFME extraction setup

These developed methods were then compared to a SPE method with Oasis MAX cartridges [3], in terms of enrichment factors, linearity, repeatability, extraction time, volumes of solvents used and ease of handling.

Matrix effects and process efficiency were also evaluated for all methods in the environmental matrix of river water. The analytes were determined in Slovenian river and wastewater samples.

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P 1

ISOLATION AND DETERMINATION OF SUGARS AND SUGAR ALCOHOLS FROM CONIFEROUS FOLIAGE

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Carbohydrates are probably the most common organic substances in nature. Sugars and sugar alcohols play an active role in regulation of growth, photosynthesis, carbon partitioning, carbohydrate and lipid metabolism, osmotic homeostasis, protein synthesis and gene expression during various abiotic stresses. A large number of sugars and polyols have great biological activity not only in relation to microorganisms and plants, but also to the human body. Many kinds of polysaccharides have been reported to have anti-tumor activities. Also, a large number of plants have biological activity for the treatment of diabetes and antioxidant activity due to the presence of these compounds.

The ultrasound assisted extraction method for isolation of 17 sugars and sugar alcohols from coniferous plants with a subsequent hydrophilic interaction chromatography-tandem mass spectrometry method for their determination were developed. The optimization of extraction parameters was carried out using Taguchi Method – L_9 (3^4) orthogonal array experimental design for the following parameters: methanol concentration in the extraction solution, extraction time, type of plant fraction and extraction temperature. The optimal ultrasound assisted extraction conditions were: MeOH concentration – 30 % (water – 70 %), extraction time – 30 min, plant fractional type – II (ground with a blade to the size of needles from 2 to 4 mm), extraction temperature – 60 °C. So, it was shown in the work that using mass spectrometric detection and LC separation amide columns can achieve record low detection limits and excellent analytical characteristics of the method without derivatization. Further, the degree of extraction of analytes from the plant material was determined by multiple successive extraction method to confirm the results. The accuracy for all studied extraction technique and chromatographic separation was confirmed by spiking of the plant material with standards before extraction and HPLC-ESI-MS/MS analysis and the analytical method was validated for linearity, limits of detection, limit of quantification, precision and accuracy.

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P 2

A NOVEL METHOD FOR DETERMINING PBDE AND PCB IN LIPOPHILIC MATRICES BY MS/MS AND HRMS

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Introduction

Levels of polybrominated biphenyl ethers (PBDEs) in the environment and in biological objects are studied more than 20 years, generally accepted methods are still lacking, limited laboratories detect heavy-PBDEs and very few can analyze Mono- and DiBDEs. PBDEs being similar in structure to polychlorinated biphenyls (PCBs), a certain similarity in their analytical chemistry might be expected. However, this is only true for medium-brominated compounds, which are the most popular objects of PBDE analysis. The purpose of this work was to develop a viable method for simultaneous determination of mono- to decabromobiphenyl ethers and indicator and dioxin-like PCBs in fat samples.

Material and methods

The analyses were performed on a Thermo TSQ8000Evo/Trace1310GC triple quad system in MS/MS mode, Thermo TR-5MS column and on Waters AutoSpec Premier with Thermo TR-5MS, SGE-HT8 and J&W DB-5ms columns. The following sorbents were used: Aluminum oxide, basic, Brockman I (Sigma-Aldrich); Aluminum oxide activated, neutral, Brockmann I (Sigma-Aldrich); Aluminum oxide, Type WN-6, Neutral, Activity Grade Super I (Sigma-Aldrich); Florisil (0.150-0.250) (Merck); Florisil PR (Merck); silica gel impregnated by sulfuric acid and potassium silicate were prepared from Silica gel 60 (0.063-0.100 mm) (Merck).

Results and discussion

We tested different sorption systems in order to find a good quality cleaning with reasonable solvent consumption and low blank contamination. As a result, we found the system (Fig. 1) with the following benefits:

- all PBDEs congeners (from mono- to deca-) as well as indicator and dioxin-like PCBs in same extract;
- low blank level (<1 pg for most abundant PBDE congeners);
- stable and high recovery (at least 80%);
- low consumption of halogen-free solvents (110 ml per sample);
- easy to use

Unfortunately, there are no chromatographic columns that are suitable for elution of heavy PBDE and capable of separating indicator PCBs from other isomers. Therefore, in general, it is necessary to carry out the analysis on two columns; but PCBs and low brominated PBDEs (at least to hexa-) could be analysed in same injection on SGE HT-8 column (8% Phenyl (equiv.)

Polycarborane-siloxane). The analysis can be performed both on a "classical" HRMS system, so by the MS/MS on triple quadrupole. Both systems provide sufficient sensitivity, but MS/MS provide a little bit better chromatograms, since there are no interference between PeCB (325.8804/327.8775) and DiBDE (325.8941/327.8921) ions.

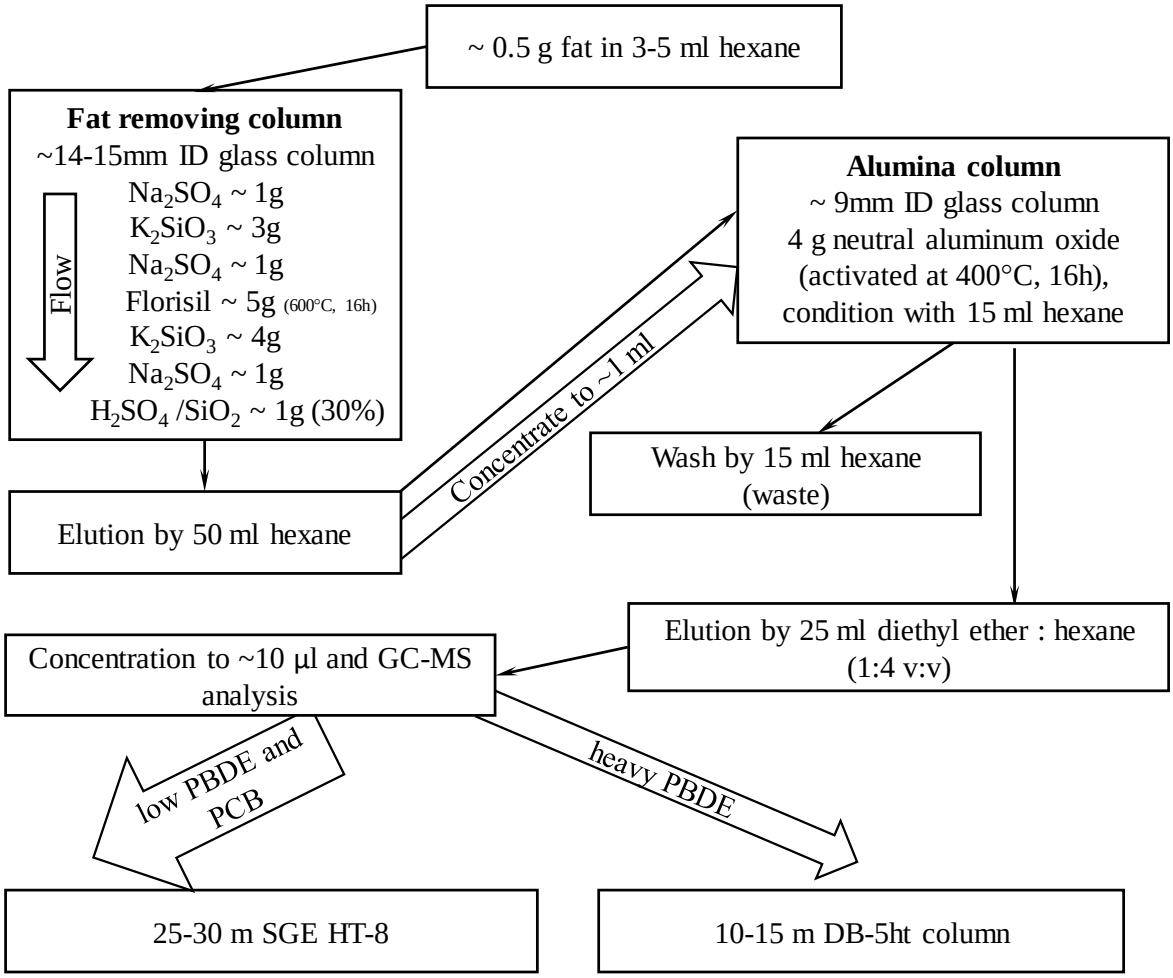

Fig. 1. A flow chart for PBDEs and PCBs clean-up in the analysis of lipophilic matrices

P 3

DEVELOPMENT OF BIO-ENERGY IN GEORGIA

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Development of bio-energy is one of the main trends of world fuel industry today. The threat of limited reserves of hydrocarbons prompted the International Energy Agency to declare development of bio-energy as the mainstream of world fuel market, which marks a new era in energy industry worldwide.
Bio-fuel, as alternative fuel, is based on processing of bio-resources; the main sources for biodiesel production are considered plant oils, such as rapeseed, soybeans, peanut, palm, corn, sunflower, olive, etc). Even though usage of biodiesel may trigger a slight decrease in fuel economy, the main advantage is that biodiesel is carbon-neutral, bio-degradable and less toxic; it also extends the life of diesel engines. Biodiesel is one of the most environmentally friendly fuels, it significantly reduce harmful emissions, including carbon monoxide and carbon dioxide.

We have studied and analyzed several sources for biodiesel production from rapeseeds (*Brassica napus*) grown in Georgia, as well as secondary (cooking) oil from food industry. From these bio resources, trough the process of etherification with methanol using small scale, pilot machinery for bio-diesel production, we have received pure biodiesel fuel B100 and free glycerin as by-product. We have analyzed physical and chemical characteristics of B100, as well as several other composites of biodiesel blend with petroleum diesel fuel (B10 and B20).

The composition of fatty acids in B20 and B100 has been studied using a liquid chromatographer and the functional groups were analyzed by Spectrum Two spectrometer. The conducted analyses and results have clearly demonstrated that the physical and chemical parameters of both B100 and B20 were within the standards of EN 14214, ASTM D6751 and EN 590. Based on the results of our research we have started regular production of biodiesel fuel, which now is being tested in the engines of the municipality vehicles of the city of Tbilisi, Georgia. The by-product, glycerin is used for production of washing foams.
Based on our research and findings we have defined a new nano-composition of biodiesel fuel with the aim to improve technical parameters of this fuel to ensure better performance of diesel type internal combustion engines without any modification of the engines design.

P 4

MASS SPECTROMETRIC STUDY OF TAR-ASPHALTENE SUBSTANCES OF GEORGIAN OILS

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When studying high-boiling compounds of oil that are characterized by an extremely complex composition and a wide variety of molecules in them, methods for detection and identification of polycyclic condensed aromatic systems that are known to be the main structural blocks of tar-asphaltene substances of oils are of particular interest.

To study these tar-asphaltene systems of oil we used elaborated in our laboratory method of hydropyrolytic fragmentation of hydrocarbons. The prospectivity of the autoclave hydropyrolysis method for determination of aromatic fragments of tar-asphaltene substances was studied using oils of different chemical nature from Supsa (resinous), Samgori (paraffinic) and Norio (aromatic) oil deposits.

Hydropyolysates of tars and asphaltenes were analyzed by gas-liquid chromatography (GLC) and mass spectrometry. GLC analysis of hydropyolysates of tars and asphaltenes showed that they are almost identical by composition, contain the same aromatic structures and differ from each other only in terms of the quantitative ratio of these structures. Composition of hydropyolysates was determined by peaks of molecular ions, taking into account the correction for the natural occurrence of the ^{12}C and ^{13}C isotopes and for the relative sensitivity coefficients reflecting relative probability of formation of ions for different compounds.

Mass spectrometric analysis of the hydropyolysates of the test samples shows that they contain the same structures. The identified structures were: naphthalenes, biphenyls, fluorenes, phenanthrenes, pyrenes, chrysenes, perylenes, benzochrizenes, benzperylenes. The higher content of phenanthrenes, pyrenes, chrysenes and perylenes was noted. There are also a lot of aromatic structures with large number of rings in the condensed system, although the main part of them are compounds with the degree of hydrogen unsaturation C_nH_{2n-x} up to x = 30.

Thus, the results of the study of hydropyolysates of tar-asphaltene substances of oil show that their main aromatic fragments, regardless of the chemical nature of oils, are the same aromatic structures, mainly with the degree of hydrogen unsaturation C_nH_{2n-x} up to x = 30.

P 5

FRAGMENTATION OF PYRIDINIUM PRE-FORMED IONS AND ZWITTERIONS — DOES THE FORMAL POSITIVE CHARGE REMAINS WHERE IT IS DESIGNATED?

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Pre-formed cation derivatives including pyridinium salts are widely used to enhance sensitivity of analysis of alcohols, phenols, carboxylic acids and some other low-molecular organic substances by ESI MS and MALDI/SALDI MS. However, little is known about fragmentation of these derivatives. The problem of location of the positive charge after CID fragmentation has no evident solution: the charged fragment may be formed from pyridinium where the sign "plus" is written (proton migration) or from the opposite part of the molecule (charge migration). For three pyridinium ribosides, CID in IT gave pyridinium cations only ("plus" remained as it was located) [1]. We have studied neopetrosides A (2) and B (7) [2] and their analogs (Fig. 1) using high-resolution QqToF instrument. Both pathways can be realized (in parentheses). 1. The main fragment ion is formed from the "plus-tagged" part, *i.e.*, pyridinium ion, aglycone, or its further decomposition. 2. The main fragment ion is related to the alternative part of the molecule, *i.e.*, this is the glycosyl oxonium ion. Thus, the fragmentation pathway of pyridinium glycosides depends on the structure of the glycosidic part, activation energy, and the associated ion (for zwitterions).

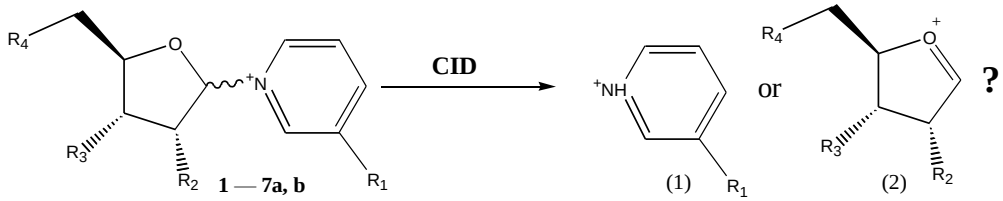

Fig. 1. Py: pyridine cycle, Pyr: pyrrole cycle

1. R_1 = $CONH_2$, R_2 = R_3 = R_4 = OH (alpha anomer) (1) (cf. [1])
2a: R_1 = COOH, R_2 = R_3 = OH, R_4 = (4-OH)C_6H_4COO, (alpha anomer) (2)
2b. R_1 = COONa, R_2 = R_3 = OH, R_4 = (4-OH)C_6H_4COO, (alpha anomer) (1)
3a: R_1 = COOH, R_2 = R_3 = OH, R_4 = (4-OH)C_6H_4COO, (beta anomer) (2)
3b. R_1 = COONa, R_2 = R_3 = OH, R_4 = (4-OH)C_6H_4COO, (beta anomer) (1)
4. R_1 = $COOC_2H_5$, R_2, R_3 = $(H_3C)_2C(O)O$, R_4 = (4-AcO)C_6H_4COO (alpha anomer) (2)
5a. R_1 = COOH, R_2, R_3 = $(H_3C)_2C(O)O$, R_4 = (4-HO)C_6H_4COO (alpha anomer) (2)
5b. R_1 = COONa, R_2, R_3 = $(H_3C)_2C(O)O$, R_4 = (4-HO)C_6H_4COO (alpha anomer) (2)
6a. R_1 = COOH, R_2, R_3 = $(H_3C)_2C(O)O$, R_4 = (2-Pyr)COO (alpha anomer) (2)
6b. R_1 = COONa, R_2, R_3 = $(H_3C)_2C(O)O$, R_4 = (2-Pyr)COO (alpha anomer) (2 for 25 eV, 1 for 35 eV)
7a. R_1 = COOH, R_2 = R_3 = OH, R_4 = (2-Pyr)COO (anomer) (2 at 10 and 15 eV, 1 for 35 eV)
7b. R_1 = COONa, R_2 = R_3 = OH, R_4 = (2-Pyr)COO (anomer) (1)

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P 6

DIFFERENTIATION OF TWO ISOMERIC CYCLIC TETRASACCHARIDES BY ESI CID MS/MS

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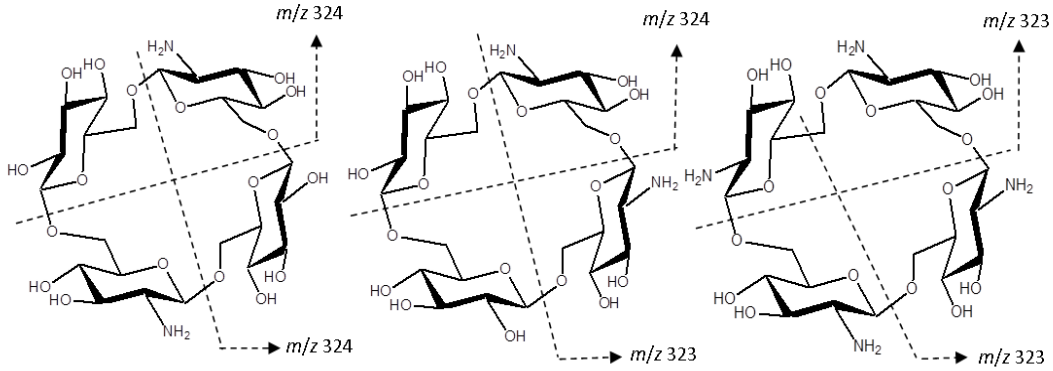
Previously, we reported the synthesis and conformational studies of cyclic □-(1□6)-D-glucosamino oligosaccharides possessing unusual properties [1]. Two isomeric cyclic tetrasaccharides, cyclobis-(1□6)-(□-D-glucopyranosyl)-(1□6)-(2-amino-2-deoxy-□-D-glucopyranosyl) **1** and cyclo-(1□6)-(2-amino-2-deoxy-□-D-glucopyranosyl)-(1□6)-(2-amino-2-deoxy-□-D-glucopyranosyl)-(1□6)-(□-D-glucopyranosyl)-(1□6)-(□-D-glucopyranosyl) **2** [2] have minor differences in their ESI CID MS^2 of $[M+2H]^{2+}$ and $[M+H]^+$ ions: disaccharide fragments of **1** are equal (m/z 324, not m/z 323), whereas analogous cleavages of opposite glycosidic bonds in **2** give two of three possible disaccharide fragments (m/z 323 and m/z 324, Fig. 1). For comparison, cyclotetrakis-(1□6)-(2-amino-2-deoxy-□-D-glucopyranosyl) **3** affords prominent peak at m/z 323 under CID MS^2 [3].



1 **2** **3**

Fig. 1

Literature.
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P 7

SIMULTANEOUS DETERMINATION OF THE MOST PRESCRIBED ANTIBIOTICS IN DRINKING WATER BY LC-MS/MS

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Antibiotics are chemical substances with biological activity against some microorganisms being considered the most productive family of drugs so far developed for ameliorating human health. Besides this basic application, antibiotics are used for preventing and treating animals, different plant infections and also for advancing the growth in animal farming. The antibiotics in Serbia are consumed five times more than in the European Union and unfortunately they often end up in the natural water courses. The widespread occurrence of antibiotics as contaminants in the aquatic environment has increased the attention over the past years. The concern over the release of antibiotics into the environment is related primarily to the potential for the development of antimicrobial resistance among microorganisms. A rapid analytical method was developed for the determination of three antibiotics: azithromycin, clarithromycin, erythromycin in water. The analytical method is the combination of a low-sample-volume solid phase extraction (SPE), followed by a chromatographic separation using a reversed phase (RP) and liquid chromatography coupled to a triple quadrupole mass spectrometer (LC-MS/MS). The detection was performed with the multiple reaction monitoring (MRM) measured with positive electrospray ionization (ESI+). The extraction of antibiotics was obtained by the Bond ElutPlexa, 60 mg, 3 mL. The squared coefficient of the determination (R^2) in the concentration range (0.005-0.05 ng/mL) of the calibration curves for the method was higher than 0.99 for all investigated antibiotics. The limit of quantification (LOQ) was established to 0.005 µg/L for all of them. The recoveries ranged from 76% (erythromycin) to 92% (clarithromycin) using the standard addition approach for the calibration and internal standard trimetophrim-D9. The LC-MS/MS analysis of 18 drinking water samples (collected from the locality of the city Belgrade, Serbia from the beginning of 2018 till now) showed no antibiotics detection over 0.005 µg/L.

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P 8

POST-CHROMATOGRAPHIC DERIVATIZATION APPROACH FOR ANALYSIS OF STEROLES BY TLC/MALDI

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Versatility, cheapness and rapidity of thin-layer chromatography (TLC) provide an important place of this method in qualitative and semi-quantitative analysis of a variety of compounds. The main drawback of TLC is the lack of informativity and selectivity of traditional methods of identification based on chemical and optical approaches or R_f (retardation factor) values. One of the most promising ways to overcome these disadvantages is to apply mass spectrometry methods to detect analytes resolved by TLC. Mass spectrometric desorption/ionization methods, such as matrix-assisted laser desorption/ionization (MALDI), seem to be the most suitable for this purpose because of a possibility to ionize analytes directly from TLC plates. At the same time non-polar or low-polar compounds often do not undergo ionization processes in MALDI conditions. The simplest approach allowing to use 'soft' mass spectrometric methods for analysis of these compounds is based on different derivatization techniques. Products of such reaction readily ionize in MALDI and other 'soft' ionization conditions providing intense peaks of corresponding ions. Herein we describe application of post-chromatographic derivatization approach for analysis of sterols by TLC/MALDI.

The proposed approach is based on of modification of alcohols by their acylation by acyl halides of halogen-substituted fatty acids with simultaneous quaternization by nitrogenous bases. Resulting salts have high desorption/ionization efficiencies in MALDI conditions and very low TLC mobility. This fact does not allow using the method for developing of pre-chromatographic derivatization procedures. At the same time, the process is exothermal and does not require any heating or other treatment of the reaction mixture. These qualities make the approach suitable for post-chromatographic derivatization. The approach was tested using of sterols presenting in vegetable oils. MALDI mass spectra were registered directly from TLC plates and contained intense peaks of corresponding derivatives.

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P 9

DETERMINATION OF PHARMACEUTICALS IN WASTEWATERS BY DIRECT HPLC-MS METHOD

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The rise of pharmaceutical consumption worldwide makes absolutely essential the intensive study of their occurrence in the environment along with their short-term and long-term effects. Consequently, advanced analytical methods are required in order to monitor the presence of pharmaceuticals in wastewater, surface water, and drinking water. Especial attention is paid to the control of trace amounts of pharmaceuticals in wastewaters of the pharmaceutical companies and in nearest regions.

A fast and sensitive approach for multiclass analysis of 20 different API (Active Pharmaceutical Ingredients) was developed and validated. Analysis of wastewater samples was performed by direct injection into the LC/MS system without the need for a preceding enrichment step. The separation was achieved on Gemini-NX C18 column using mobile phase of 20 mM ammonium acetate with pH 4.0 and acetonitrile in gradient mode. Simultaneous detection in both positive and negative mode using HESI source allowed to determine all the analytes with high selectivity in less than 15 minutes.

Precision, expressed as relative standard deviations, was always below 5%, and the method detection limits ranged from 100.0 ng/L (Meldonium Dihydrate) to 10.0 ng/L (Zoledronic Acid).

The developed technique was introduced into practice of QC department of pharmaceutical company Bion for routine control of wastewater samples according to GMP requirements.

P 10

CHEMICAL CHARACTERIZATION OF OLIVE OIL MILL WASTE MATRIX AND SUBFRACTION: SPECIES SPECIFIC TOXICITY STUDY

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The production of olive oil yields a considerable amount of olive mill wastewater (OMW) as a by-product of olive oil extraction process, which is currently discarded throughout the Mediterranean region. It is estimated that $7x10^6$ – $3x10^7$ m^3 of OMW is generated annually, which is alarming considering that this type of pollution is equivalent to the pollution of municipal wastewater produced by 20-22 million people. OMWs significant polluting properties are mainly related to high organic load, increased COD/BOD ratio, high phenolic content and relatively acidic pH. Currently, there is no strict regulation or appropriate method applied for treating OMW. It is usually discharged into sewage systems and/or into different environmental compartments. There is no data concerning the level of OMW in the receiving waters, but considering that the approximated amount of 1.5 million tons of untreated OMWs are annually disposed in a short period, it is obvious that OMW are becoming a potential environmental issue. Previous toxicity evaluation of OMWs were mostly based on one-way research, which contributed to the lack of studies using a battery of ecotoxicological assays with model organisms from different trophic levels and with different sensitivities. The main goal of this study was to evaluate (sub)lethal effects of OMW to different model organisms: *Vibrio fischeri*, *Chlorella vulgaris*, *Dapnia magna*, *Danio rerio*, *Trifolium repens* and *Triticum aestivum*. Identical bioassays were performed with raw sample and subfraction in order to determine in which amount polyphenols are responsible for the OMWs toxicity. Moreover, analysis of organic compounds within the subfraction was carried out using gas chromatography–mass spectrometry and high resolution mass spectrometry. Obtained results identified tyrosol as the most common polyphenol, and showed a clear correlation between polyphenols concentration and observed toxicity. These findings may contribute to the understanding of OMW induced toxicity on primary producers (plants, invertebrates and vertebrates) and its potential environmental effects.

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P 11

BIOSORPTION OF Ag NANOPARTICLES FROM WASTE WATERS BY BREWER'S SACCHAROMYCES YEAST BIOMASS

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Nano technology is one of the most widely applied technologies in all branches of humans' lives from pharmaceuticals, cosmetics, textiles, coatings, catalysts, etc. Not only our future, but already our reality is full of new emerging pollutants, where nano materials, because of their physical properties and elevated production, are one of the most important player in preventing or causing new environmental outcomes.

In this study the capacity of silver nanoparticles (AgNPs, 50 nm) removal from wastewaters with spent brewer´s yeast biomass composed of *Saccharomyces cervisiae* (heat-killed at 45 ˚C) was studied regarding to the pH of wastewaters (pH 5 or pH 8). The re-use of agro-industrial by-products from economical to ecological point of view is a significant achievement for chemical free waste water treatment technologies (WWTT). Their flocculation ability, showed a promising capacity for AgNPs removal (from 20% to 75%) at pH 8, only. Whereas at pH 5, the addition of yeast caused the transformation of AgNPs into soluble form of Ag^{+} ions.

The solutions were all analyzed by single particle inductively coupled plasma mass spectrometry (spICP-MS) (NexIon 350X, Perkin Elmer, USA). The solutions were sonicated for 5 minutes and diluted in order to obtain a final concentration of AgNPs in the range of 1000 to 20.000 particles per ml. The spICP-MS parameters were set as follow: Dwell Time 100 µs, Sample Time 100 s, the Sample Flow Rate and the Transport Efficiency were daily calculated. The sample flow rate was obtained by aspirating MilliQ water for 5 minutes and checking the weight difference, while the transport efficiency was determined by using gold nanoparticles standards (AuNPs) of 30 and 80 nm size and gold dissolved solutions at 1, 2, 4 and 10 ppb, respectively.

The application of yeast as a biosorbent is a promising way of metals and nanoparticles removal from wastewaters and it also eases the burden costs associated with waste management.

ACKNOWLEDGEMENTS (Slovenian Research Agency, P3-0388, Mechanisms of health maintenance).

P 12

COMPLEX APPROACH FOR POLAR HERBICIDES DETERMINATION IN OILSEEDS, CEREALS AND HONEY BY HPLC-QTOF

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Glyphosate (Gly) and glufosinate (Glu) belong to broad-spectrum systemic herbicides group. These compounds are widely used for weed control on fields. It is very important to know, that Gly and Glu are used not only for GM organisms, but also for original cultures (at soil remediation stages). Application of these herbicides results in broad contamination of different crops and all food chain. One of the most important degradation products of Gly is aminomethylphosphonic acid (AMPA). Determination of Gly, Glu and AMPA by ESI-MS/MS technique is very difficult due to their small molecules and zwitterionic structures, but it is the only way to do it in accordance with Council Directive 96/23/EC (2002/657/EC). One of the consequences of Gly usage is contamination of apiculture products. Bees intoxicated by Gly, lose the ability to find food and their colony, that causes their death. Bee's population protection is a very important for future successful existence of pollination processes. The study describes efficient extraction of Gly, Glu and AMPA from oilseeds, cereals and honey followed by cleanup, derivatization step and determination of reaction products by HRMS in negative ionization mode. The sample preparation procedure is the following: sample is mixed with deionised water and hydrochloric acid for 30-60 minutes, followed by ultrasonic bath treatment. The mixture is centrifuged, an aliquot is transferred on SPE column. First aliquot is discarded; next 1 ml aliquot is collected for derivatisation step. 1 ml of borate buffer and 1 ml of FMOC-Cl are added to 1 ml of purified extract for derivatization at 50 ^{0}C for 30 min. The extract is concentrated and diluted to 2 ml with deionised water. Following SPE on MCX sorbent, the extract is concentrated and diluted to 1.0 ml with 1 % acetic acid. HPLC separation was carried out on ACQUITY BEH C18 column in gradient mode from 20 mM ammonium acetate in water to 20 mM ammonium acetate in methanol. Detection was performed on Maxis (Bruker) mass-spectrometer. The characteristic ions were 168.01, 149.99 and 124.02 m/z for Gly-FMOC; 135.98 and 110.00 m/z for AMPA-FMOC; 206.02 and 180.04 m/z for Glu-FMOC. The LOQs of described method for Gly, Glu and AMPA in honey are 0.01, 0.4 and 0.05 ppm, respectively. The LOQs in oilseeds, cereals are 0.1, 0.4 and 0.4 ppm, respectively.

P 13

NEW PRODUCTS OF OXIDATIVE TRANSFORMATION OF 1,1-DIMETHYLHYDRAZINE

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In recent decades 1,1-dimethylhydrazin (UDMH) has been widely used as rocket fuel, and it is still using in some countries. A huge amount of this compound is stored in the storage tanks. This compound can interact with air and oxygen as a result of exploitation and after violation of storage conditions these storage tanks with UDMH. Thus, because of high reactivity of UDMH, mixtures of complex composition including a number of highly toxic compounds are formed.

In this research samples of washing water from fuel tanks have been investigated. These samples contain mixture of complex composition consisting of products of oxidative transformation of UDMH. In this research a search of polar nitrogen-containing compounds (that are potentially highly toxic) has been carried out. For this purpose, the mixture was analyzed by HPLC (high performance liquid chromatography) and high-resolution mass spectrometry with ESI (ionization by electrospray).

Among the separated substances five compounds were identified as N,N-dimethylaminomethylidenamino substituted methyltriazoles. Three of them were isomers with one nitrogen-containing substituent and two others compounds were isomers with two nitrogen-containing substituents.

The structure of all these compounds has been investigated by the method of nuclear magnetic resonance (NMR) and has been confirmed by fragmentation of tandem mass-spectrometry and infrared spectroscopy. The most probable structures of isomers have been determined by 2D-NMR. Concentration of these substances in the initial mixture has been estimated by HPLC-MS using similar triazole derivatives as internal standards.

For all these compounds cytotoxicity has been investigated *in vitro*, the corellation of toxicity and the structure of compounds has been shown. A possible mechanism of formation of these compounds during oxidative transformation of UDMH in the presence of oxygen of air and water has been offered.

P 14

APPLICATION OF IONIC LIQUID MATRICES FOR OBTAINING MALDI QIT-TOF MASS SPECTRA OF LIGNIN

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In this work we propose the new approach to obtaining mass spectra of lignin based on the hybrid quadrupole ion trap – time-of-flight mass spectrometry technique and ionic liquids (ILs) as MALDI matrixes. ILs possess the high dissolving power towards lignin giving the homogenous solutions which readily absorb laser radiation and promote desorption/ionization process.

Thirty two ILs were synthesized using the common MALDI matrix anions (ferulate FA, 3,5-dihydroxybenzoate DHB, sinapinate SA, α-cyanohydroxycinnamate CHCA) and eight nitrogen containing cations (isopropylmethyl-tert-butylammonium IMTBA, butylmethylimidazolium BMIm, diisopropylethylammonium DIEA, tributylammonium TBA, pyridinium PY, methylimidazolium MI, tetramethylhydrazinium TMG, 3-aminoquinolinium AQ). It was shown the most of them are able to ionize lignin and DIEA FA, PY DHB, IMTBA CHCA allow to obtain high quality and intense spectra in the *m/z* range 800-2500 with fine structure reflecting the nature of lignin preparations studied. The full suppression of matrix cluster signals in mass spectra with lignin is observed.

The combination of IL MALDI with QIT-TOF mass analyzer provides the possibilities to record MS^n spectra of selected precursor ions (even with *m/z* > 2000) allowing to obtain more structural information based on collision induced dissociation of lignin oligomers. The simple approach to discrimination of different types of lignins based on their MALDI MS/MS spectra was developed.

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P 15

ULTRAHIGH-RESOLUTION ORBITRAP MASS SPECTROMETRY AS A TOOL FOR STUDY OF NATURAL AND INDUSTRIAL LIGNINS

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Due to the limited elemental compositions of natural lignins (CHO-class) the reliable determination of gross formulae of lignin oligomers does not need the very expensive Ion cyclotron resonance mass spectrometry and can be successfully done by the method of Orbital ion trap MS which allows to achieve the spectral resolution up to 500 000 FWHM and mass accuracy better than 1 ppm using the benchtop instruments.

It is shown that use of atmospheric pressure acetone or dioxane-doped photoionization in combination with high-resolution Orbitrap MS provides the detection of about 2000 oligomers with masses up to 2 kDa in softwood dioxane lignin preparation and up to 10 000 oligomers in the products of lignin solvolysis.

The study of the component composition of monomeric fragments of macromolecules, obtained as a result of collision induced dissociation of lignin oligomers in wide mass range, allows an rapid assessment of the features of the functional composition and nature of various lignin preparations.

The involvement of chemometric methods for high-resolution mass spectra processing, as well as visualization of data on elemental compositions of oligomers by van Krevelen's method, opened the possibilities for comparing lignins of various origin and studying their transformation in natural and technical processes.

The successful application of Orbitrap MS to control the processes of depolymerisation of alkali lignin in supercritical media is demonstrated.

This work was performed under financial support of Russian Foundation for Basic Research (grant No. 17-43-290657) and Ministry of Education and Science of Russian Federation (project 4.2518.2017/4.6)

P 16

NON-TARGETED SCREENING OF UNSYMMETRICAL DIMETHYLHYDRAZINE TRANSFORMATION PRODUCTS BY HIGH-RESOLUTION MASS SPECTROMETRY

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Unsymmetrical dimethylhydrazine (UDMH) is used as a propellant (in combination with nitrogen tetroxide as an oxidizer) for some classes of rockets, including heavy carrier rocket "Proton". Being highly reactive substance, UDMH when released into the environment gives a wide range of toxic and carcinogenic products of its oxidative transformations. Their reliable identification and screening in environmental objects is a challenging task requiring the application of modern methods of high-resolution mass spectrometry.

We used Orbitrap mass spectrometry with electrospray ionization for monitoring of reactions of UDMH oxidation with different reagents and characterization of the products formed on the basis of their elemental compositions. The results obtained demonstrate that the oxidation of UDMH proceeds in two stages with the formation of a great number of complex unstable intermediates, containing up to ten nitrogen atoms and converting into final reaction products with a decrease in the average molecular weight (from 104 to 92 Da). The overall number of nitrogen-containing oxidation products exceeds 200 and can achieve one thousand. The following classes of heterocyclic compounds were found among them: pyridines, imines, piperidines, pyrrolidines, dihydropyrazoles, dihydroimidazoles, triazoles, aminotriazines, and tetrazines.
Taking into account the presence of a great number of isomeric species the preliminary separation is required for the purposes of untargeted mass spectrometry screening of UDMH transformation products in soils. The solution of this task was achieved by the UHPLC-ESI-Q-TOF MS method with chromatographic separation of analytes on a porous graphitized carbon stationary phase (Hypercarb). It allowed us to obtain new data on the pollution of soils in the falling places of spent rocket stages in Kazakhstan and Northern Russia.

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P 17

IDENTIFICATION OF SHALE OILS FROM THE BAZHENOV FORMATION USING GCXGC-MS

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Recent studies of oil composition using modern GC-MS, GC-MS/MS, GCxGC-MS, FTIR and other analytical instruments shows that each well has a unique hydrocarbon fingerprint even within a small geographic area. It allows petroleum engineers to apply hydrocarbon fingerprinting for solving complicated problems in oil recovery.

This research is objected to analysis of 9 shale oils from the Lower Jurassic to the Upper Cretaceous Bazhenov Formation sampled in different oilfields of West Siberian petroleum basin, Russia. Studied oilfields are characterized by different level of kerogen maturity from the beginning of oil window zone to the latest stages of hydrocarbon generation.

GCxGC-TOFMS Pegasus 4D (LECO) instrument was applied for analysis of chemical composition of oils (maltenes hexane solution). GCxGC-FID data was essential for correct calculation of indexes based on relative content of organic compounds of different classes. Natural variations of isotope composition of C, H, S, N and O in oil samples and fractions, and also in individual alkanes and isoprenoids were studied using IRMS (Delta V Plus).

With the lack of relative concentration of hopanes in studied samples, the following parameters shows distinct decrease with maturation: isoprenoid index (Ki) has values from 0.6 to 0.3; 1/(1+4)-MDBTs and DBT/1-MDBT ratios linearly drop from 0.5 to 0.04 and 1 to 0.03, respectively, as DBT concentration increases with thermal degradation, and its methylation does not occur for type II kerogen [1]. Isotope composition of oil samples varies from -32.1‰ to -30.5‰ PDB for carbon and from -155‰ to - 140‰ SMOW for hydrogen. Enriched in O18 and D samples are corresponded to higher level of kerogen maturation.

Thus, accordingly to obtained results, chemical and isotope composition of oil samples varies in a considerable range of values, depending first of all on kerogen maturation and also on some other parameters of petroleum basin. Obtained results show that oil fingerprinting based on GCxGC-TOFMS and isotope ratios study could be applied for number of tasks of reservoir geochemistry including oil fingerprinting, reservoir connectivity, evaluation of kerogen maturation and others.

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P 18

IMPORTANCE OF STABILITY STUDIES OF UV FILTERS FOR ERITEMA ASSESSMENT AFTER EXPOSURE TO UV LIGHT

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It is already known that the photostability of sunscreen products (SCP) is important for complete human skin protection. Skin in fact, is naturally protected from photodamage by its antioxidants, but when there is excessive sun exposure, the body may not be able to completely neutralize the free radicals generated by UV exposure, which consequently can lead to many cell damages. For this purpose the use of sunscreens containing organic UV filters is needed to protect the skin from UV-induced damage. However, the protection is not ideal because of inadequate use, incomplete spectral protection, filter degradation and toxicity.

The main objectives of the present study were thus, to elucidate the photo-induced products of a commonly used filter - avobenzone in chlorinated waters on the toxicity of photostimulated avobenzone present in 3 commercial sunscreen products and in its original pure form.

Chlorination experiments of sunscreens were performed with OAISIS® water purification tablets by Hydrachem, while photo-degradation experiments were performed in a custom-made photoreactor with 4 UVA lamps (CLEO 20 W, 438 mm × 26 mm, Philips; broad maximum at 355 nm) and 2 UVB lamps (CLEO 20 W, 438 mm × 26 mm, Philips; broad maximum at 355 nm) equipped with 4 quartz glass cell with the effective volume of 100 mL.

For the kinetic studies, the solutions were irradiated for fixed periods of time (0, 15, 30, 60 min) and analysed by HPLC-DAD (UV-Vis). Whereas, the identification of photo-products was performed by Waters/Micromass LC/QTOF tandem MS with an orthogonal geometry Z-spray ion source, for LC/ESI/MS and LC/ESI/MS/MS experiments. The toxicity of irradiated and chlorinated samples was measured by the inhibition of marine bacteria *Vibrio Fisheri.*

Avobenzone in SFC and in pure form was similarly resistant to the UVA/UVB irradiation after one hour of irradiation. The chlorination (both dark experiment and UVA/UVB irradiation) of solutions had an immediate effect on the concentration of avobenzone in pure form, whereas it has little effect on avobenzone in SCPs' formulations, which expressed a protection of the avobenzone in the complex solution of SCP. An interesting fact was noticed in case of toxicity studies, since the inhibition of *Vibrio fisheri* was raised in all cases (pure and SCPs' form) of chlorinated avobenzone compared to UVA/UVB irradiated samples. For this reason our predominant task was, to solve the question from which compound might the toxicity come. For this purpose LC/MS-MS analyes were performed. The results inticate the formation of two major chlorination products (2-chloro-1-(4-**tert**-butylphenyl)-3-(4-methoxyphenyl)-1,3-propanedione and 2,2-dichloro-1-(4-**tert**-butylphenyl)-3-(4-methoxyphenyl)-1,3-propanedione) and other substituted chlorinated phenols and acetophenones, which are known to be rather toxic.

P 19

EXPLORATION OF A NEW WASTE PRODUCT «BLACK OSMOL» WHICH IS AN OXIDISED MIXTURE OF 1,1-DIMETHYLHYDRAZINE

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1,1-Dimethylhydrazine - unsymmetrical dimethylhydrazine (UDMH) - is a component widely used in rocket fuel. Since UDMH is toxic and carcinogenic it undergoes oxidative conversion to form a mixture of wide variety of nitrogen-containing compounds, in particular “black osmol”. However, some products of the UDMH transformation have carcinogenic and mutagenic effects and refer to first class danger. The formation of transformation products such as “black osmol” take place during the washing of fuel and storage tanks.

In this research, we studied the sample of the oxidised mixture of 1,1-dimethylhydrazine which is a water solution of the contents of the storage tank where the washing water with UDMH was stored. In order to detect UDMH transformation products, HPLC-MC/MC and MALDI-MC methods were used. A comparison of different methods of mass spectrometry analysis of sample preparation was made. The compounds m/z in the range of 100-300 Da were detected. Settings for the chromatographic separation were picked and the components with the highest concentration were selected. A series of chromatography-mass spectrometric analysis was carried out to study the structure of the explored compounds.

The sorption ability of a natural material, shungite, which is used as one of the ways for the "black osmol" neutralization, was analyzed. It was evident that the sorption of low-molecular compounds of the aqueous solution of "black osmol" occurs more intensively than the sorption of high molecular compounds.

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