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XII International Mass Spectrometry Conference on Petrochemistry, Environmental and Food Chemistry
Petromass 2022
October 16-23 2022
Crete, Greece

Final Programme

October 16th, Sunday

Arrival of participants

October 17th, Monday

11.00-16.00	**Registration**
16.00-20.00	**Welcome party**

October 18th, Tuesday

10.00-10.15	**Opening ceremony**
10.15-11.00	*R.Zubarev* Proteomics-compatible Fourier Transform Isotopic Ratio Mass Spectrometry of Polypeptides
11.00-11.45	*J. Schwarzbauer* Critical aspects on offline pyrolysis-based GC/MS quantitation of microplastic in environmental samples
11.45-12.15	**Coffee break**
12.15-12.40	*C.Schwanen* Dispersion of organic contaminants during flood events on the Rur river, Germany
12.40-13.05	*I.Jovancicevic* Analysis of structurally modified polyacrylamide based flocculants by off-line thermochemolysis-GC-MS
13.05-13.30	*B.Jovancicevic* Biological markers in oil as a tool to assess the origin of oil in natural geological conditions, but also to identify and assess the fate in the environment as a polluting substance
13.30-15.30	**Lunch**
15.30-16.30	*E.Stashenko* A wonderful adventure of insects with plants in a tropical garden
16.30-16.35	*A.Gonzalez* Decarboxylation of diclofenac and formation of artefacts in the hot GC injection port
16.35-1640	*J.C.Rosero* Analysis of volatile fraction of the *Cymbopogon winterianus* (Poaceae) encapsulated essential oil
16.40-16.45	*S.M.Porras* Chemical characterization by LC/MS of secondary metabolites in hydroethanolic extracts of *Scutellaria incarnata* (Lamiaceae) and study of their antioxidant activity
16.45-16.50	*S.B.Beltrán* Chemical composition of essential oil and extract isolated from *Hyptis colombiana* (Lamiaceae)

16.50-16.55	*C.G.Quintero* GC/MS characterization of the major compounds in the essential oil and its fractions obtained from two chemotypes of *Lippia alba* (Verbenaceae)
16.55-17.00	*L.D. Burgos* GC/MS and LC/MS analyses of the secondary metabolites obtained by different extraction methods from *Varronia curassavica Jacq*. (Boraginaceae)
17.00-17.05	*D.E. Vega* Comparison of the chemical composition of essential oils distilled from a wild and a domesticated *Calea spp.* (Asteraceae) plants grown in Santander, Colombia
17.05-17.10	*S.C. Luna* Determination by UHPLC-ESI-Q-Orbitrap-HRMS of anti inflammatory compounds and their metabolites after interaction with *Salvinia adnata* in aqueous medium
17.10-17.15	*H.D.Uribe* LC/MS study of ergoline alkaloids isolated from *Ipomoea tricolor* (Convolvulaceae) seeds
17.15-17.20	*S.Ortiz* LC/MS analysis of cocaine found in a caterpillar that consumed fruits from coca plant
17.20-17.25	*D.J.Portillo* Study by GC/MS and GC/FID of *Cymbopogon winterianus* (Poaceae) essential oils from Colombia
17.25-17.30	*J.J.Tarazona* Chemical characterization by LC/MS of the extracts obtained from *Ocimum campechianum* (Lamiaceae)
17.30-17.35	*A.K.Romero* Chemical composition of essential oils and extracts isolated from plants of the genus Cymbopogon, cultivated in Colombia
17.35-17.40	*N.G.Martínez* Fractional distillation at reduced pressure of orange essential oil and obtaining of it's prins reaction product, homolimonenol

October 19th, Wednesday

10.00-11.00	*G.M.Shaidullina* Empowering improvements of LECO GCxGC-TOFMS technologies for application in Petrochemistry, Environmental and Food Chemistry
11.00-11.45	*N.Ratola* Greener approaches for the analysis of microcontaminants in several environmental matrices by GC-MS
11.45-12.15	**Coffee break**
11.50-12.15	*E.Leushina* Oil fingerprinting for unconventional reservoir samples using GC×GC-TOFMS, FT ICRMS and EA-IRMS
12.15-12.40	*E.Leushina* Reconstruction of organic matter accumulation conditions derived fromelemental, molecular and isotope composition of rocks
12.40-13.05	*P.Trebše* Doxazosin degradation with gamma irradiation
13.05-14.00	**Poster Presentations**
14.00-16.00	**Lunch**
16.00-16.15	*I.Vasileva* Rana temporaria: de novo sequencing of Arkhangelsk population skin peptides and comparison of four populations
16.15-16.30	*D.Mazur* Revealing the Urban Environmental Pollution Through Snow Analysis

16.30-16.45	*T.B.Latkin* Screening and determination of nitrogen-containing organic compounds in snow by thermal desorption gas chromatography - high resolution mass spectrometry with stir based sorptive extraction
16.45-17.00	*M.S.Popov* Thermal desorption gas chromatography – mass spectrometry determination and screening of toxic rocket fuel transformation products in sandy soils
17.00-17.15	*R.Borisov* Derivatization of small peptides for their analysis by ESI and MALDI high resolution mass spectrometry

October 20th, Thursday

10.00-10.30	*A.Lebedev* Russian Arctic environmental studies using mass spectrometry
10.30-11.00	*M.Zimens* Novel derivatization approach for detection of sulfur compounds in crude oil.
11.00-11.20	*V.Solovyeva* Evaluation of new adsorbent materials for detection of oilfield volatile hydrocrabons
12.20-12.45	*K.Vyatkina* De novo sequencing of Rana arvalis skin peptides with the Twister algorithm
12.45-15.00	**Lunch**
15.00-18.00	**Round table**
18.00-23.00	**Gala Dinner**

October 21st, Friday

Cultural activities

October 22nd, Saturday

Closing event

October 22nd, Sunday

Departure of participants

Abstracts

Proteomics-compatible Fourier Transform Isotopic Ratio Mass Spectrometry of Polypeptides

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Measuring the relative abundances of heavy stable isotopes of the elements C, H, N and O in proteins is of interest in environmental science, archaeology, zoology, medicine, and other fields. The isotopic abundance measurements of the fine structure of the immonium ions with ultrahigh resolution mass spectrometry obtained in gas-phase fragmentation of polypeptides has previously uncovered anomalous deuterium enrichment in (hydroxy)proline of bone collagen in marine mammals [1]. Here we provide a detailed description and validation of this approach and demonstrate per mil-range precision of isotopic ratio measurements in aliphatic residues from proteins and cell lysates. The analysis consists of proteomics-type experiment demanding sub-microgram amounts of protein sample and providing concomitantly protein sequence data allowing one to verify sample purity and establish its identity. A novel software tool Protein Amino Acid-resolved Isotopic Ratio Mass Spectrometry (PAIR-MS) is designed for extracting isotopic ratio data from the .raw data files acquired on an Orbitrap mass spectrometer.

1. Gharibi, H.; Chernobrovkin, A.; Eriksson, G.; Saei, A. A.; Timmons, Z.; Kitchener, A. C.; Kalthoff, D.; Lidén, K.; Makarov, A. A.; Zubarev, R. A. *Abnormal (hydroxy)prolines deuterium content redefines hydrogen chemical mass, J Am Chem Soc* 2022, PMCID# PMC8855419.

Critical aspects on offline pyrolysis-based GC/MS quantitation of micro-plastic in environmental samples

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Although pyrolytic analysis of polymers allows a quantitative determination, reports on pyrolysis-based quantifications are very scarce, most probably as the result of some critical aspects that need to be considered. This is valid especially for environmental analysis of micro-plastics that require a detection at low concentrations in complex matrices.

Therefore, an offline pyrolysis approach linked with GC/MS measurements to quantify five polymers representing the most relevant constituents of microplastics (polyethylene PE, poly-propylene PP, poly(ethylene terephthalate) PET, polystyrene PS, polyvinylchloride PVC) was studied. The analytical approach was critically evaluated and discussed covering the basic an-alytical parameters.

Offline pyrolysis-based analysis of PS and PP provided the best results with a high specificity of pyrolysis products as identified by mass spectrometry (see Fig. 1), very good reproducibility, limit of quantitation around 1 to 3 µg based on S/N ratios (without matrix effects) and a recovery from real sample matrix higher than 50%. Hence, for these synthetic polymers the presented analytical method exhibits a high potential for quantitation by GC/MS at low concentration levels in real environmental samples can be stated. Although for PE a partly lower specificity of pyrolysis products, a little lower sensitivity and reproducibility but a very good recovery from real sample matrix can be summarized offline pyrolysis -based approach seems to be applicable successfully also for PE.

Analyses of PVC and PET revealed the highest inconsistencies and drawbacks in particular regarding only minor specificity, less reproducibility and in particular the low recovery. Thus, both polymers can be quantified only with a very low degree of reliance and need complementary analysis to verify the pyrolysis-based quantitative results.

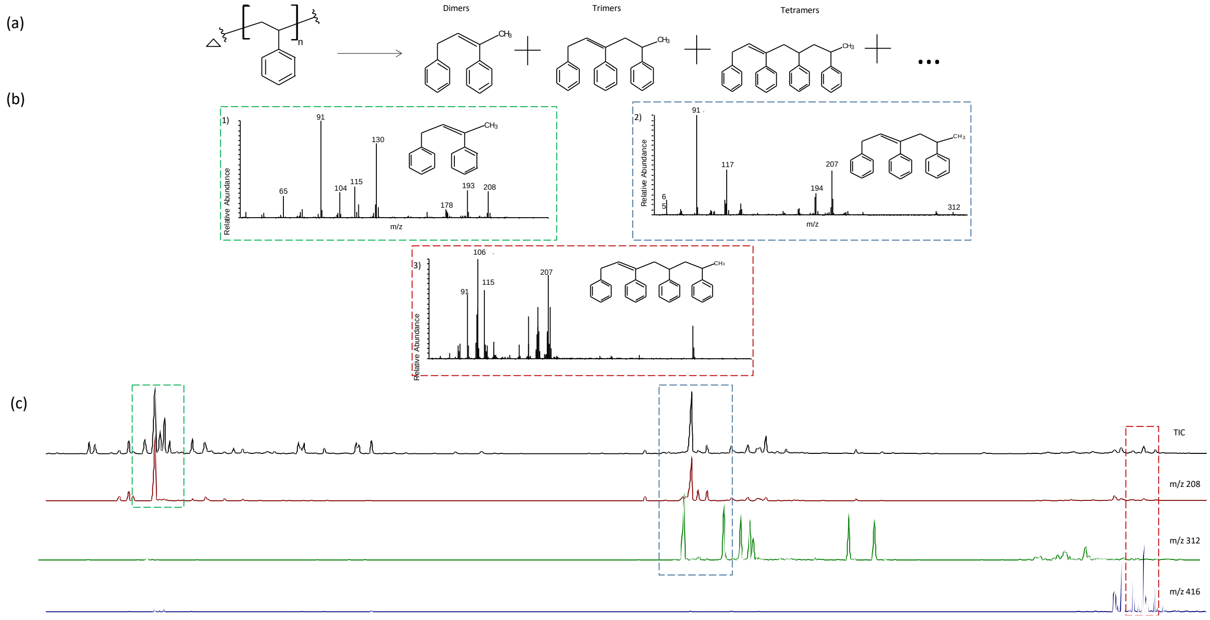

Fig. 1: Exemplified identification of specific pyrolysis products of polystyrene by GC/MS

A wonderful adventure of insects with plants in a tropical garden

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A tropical garden that we have in our research center (Industrial University of Santander, main campus, Bucaramanga, Colombia) is not very big (barely 0.5 hectares), but it is full of wonders and surprises. There are more than 500 plant species in it, including aromatic, medicinal, ornamental, edible, toxic, and magical-religious plants. It is a place full of sounds of birds and insects. In the early morning and at night the garden is filled with aromas that change their intensity and composition every hour and the concert of frogs and toads shakes the air at night. There is a biological and chemical life in the garden that is incessant and varied, very intense and of co-evolutionary relationships and survival between plants and between plants and insects. The flowers attract many insects, some during the day, but others at night; and one or another plant succumbs to the attacks of devouring ants and the caterpillars do not stop chewing the leaves. Plants are sessile organisms, they cannot move; although they are in danger, many plants manage to survive, fight, and develop different mechanisms to avoid being devoured by insects and other herbivorous animals, to overcome infections by fungi, bacteria and viruses. Some plants have thorns, others have rough bark or, on the contrary, a very smooth sliding surface, but the main weapons of plants to survive are their secondary metabolites, substances of great biological importance that participate in the ecological adaptation of plants, their resistance against herbivores, as a protection against biotic and abiotic stresses, or, on the contrary, in attracting pollinators or other insects that are natural enemies of herbivores. Many of these biological processes have chemical intermediates, molecules produced by plants, which we study at our research center. The conference will be dedicated to this and examples of volatile substances that plants emit to attract or repel insects will be given, examples will also be given of different types of alkaloids, some of them toxic, that the plant bio-synthesize for its defense, but also flavonoids and anthocyanins will be mentioned as antioxidants with different functions in both flowers and leaves. Some insects receive molecules from plants as precursors for biosynthesis of their pheromones, others consume these substances for "recreational" purposes, such as some tropane alkaloids from coca plants or *Datura* species. Analytical and instrumental methods that allow to isolate the volatile and non-volatile secondary metabolites of plants and analyze them sensitively despite their ultra-small amount will be discussed. Examples will be given of the transfer of substances from plants to visiting insects or pollinators, and to some herbivores. The journey through the tropical garden will be a chemical tale full of surprises, smells, aromas, sounds, and many colors: do not miss it.

Empowering improvements of LECO GCxGC-TOFMS technologies for application in Petrochemistry, Environmental and Food Chemistry

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Modern analytical chemists are facing more and more challenging tasks of analyzing very complex samples, detecting trace amounts of analytes of interest in the presence of high matrix, reliable identification of analytes in untargeted assays, increasing analysis throughput and more. To meet the modern challenges, LECO Corporation continuously improves the hardware and software of its products in close collaboration with scientists and implementing feedback from users around the world.

The combination of comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GCxGC-TOFMS) is a powerful method for analyzing complex samples due to the enhanced separation power and full mass range high speed data acquisition. This presentation will discuss the latest innovations recently introduced by LECO to take full advantage of this technology for Petrochemistry, Environmental and Food Chemistry.

One of the challenges facing analysts in Petrochemistry is complexity of sample, and wide concentration range of analytes, which may require often cleaning of the ion source. The LECO Pegasus BT 4D GCxGC-TOFMS source stays clean even when running large series of petroleum samples due to open design. For more advanced studies the Pegasus GC-HRT 4D instruments are preferable since high resolution accurate mass data in addition to GC×GC allow more reliable interpretation of the results using the ChromaTOF software features, which include accurate mass library search, hit list ranking by using IGS, analytes classifications, Spectral Analysis Tool, Mass Defect, Van Krevlen, and RDBE plots and more. Recently released ChromaTOF-Tile software allows statistical analysis of datasets classes.

Environmental studies often deal with samples of unpredictable composition, so the complementary ionization techniques for confident identification are advantageous. Observing molecular ions with Positive Chemical Ionization (PCI) and highlighting some classes with Electron Capture Negative Ionization (ECNI) are available with new LECO Multi-Mode Source (MMS) of Pegasus GC-HRT instrument. The benefit is the ability to perform non-target analyses simultaneously with the target analyte finding and quantification.

Food chemistry applications are related to food safety, flavor, metabolomics, product fraud forensics, and agricultural aspects. In such studies, it is usually required to detect trace amounts of target and untargeted analytes and separate them from the very complex matrix, which can be successfully performed using GCxGC coupled to subnominal or high resolution TOFMS without sacrificing acquisition speed, mass range or sensitivity. The analysis of numerous samples to determine statistically significant patterns is possible with robust instruments, reproducible data and specialized statistical software from LECO.

The use of LECO GCxGC-TOFMS instruments with LECO's software allows to obtain empowering results in the areas described above, as well as in many other applications that require comprehensive data acquisition and confident interpretation of the results.

Greener approaches for the analysis of microcontaminants in several environmental matrices by GC-MS

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Environmental analytical chemists elaborate complex protocols to be able to quantify microcontaminants from numerous matrices. However, the idea is to solve potential hazardous impacts not creating additional ones. There has been a growing awareness of the principles of Green Analytical Chemistry (GAC) that take into account this issue. In this work, we present some of the evolution and current alternatives for environmentally friendlier methods to extract microcontaminants, which in turn will also improve the resolution of the chromatographic analysis. Focus will be given to the work org group has been developing in the last years on chemicals of emerging concern (CECs) like volatile methylsiloxanes or synthetic musks in air, water, soil and vegetation, which are commonly quantified using a GC-MS equipment. The sample handling can be done by microextraction and other solvent-reducing procedures, with effective clean-up steps if required using techniques such as Quechers.

Acknowledgements

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Dispersion of organic contaminants during flood events on the Rur river, Germany

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Extreme weather events and natural disasters such as floods can cause severe destruction and impacts on natural habitats as well as anthropogenically used areas (e.g. for settlement, agriculture or industry). Thus, floods often result in the acute and unusual release, but also remobilization of various organic pollutants. The accumulation of pollutants occurs mainly on floodplains, which are of great importance during flood events due to their functions of water, sediment, and nutrient retention.

Various floodplains distributed along the course of the Rur river were sampled immediately after two different flood events in 2021. The main objective was to address the general knowledge gap on indirect effects of flooding and the corresponding dispersion of organic pollutants. Therefore, the assessment of the organic pollution in terms of concentrations, dispersion and (re)mobilization along the river course was of great relevance. All evaluations were done in the context of different dimensions and dynamics of flood events and their impact on floodplains.

Several organic pollutant groups, including PAHs (polycyclic aromatic hydrocarbons), hopanes, PCBs (polychlorinated biphenyls) and LABs (linear alkylbenzenes) were detected by a GC/MS based non-target screening. They can be used as indicators for petrogenic pollution, urban pollution (e.g., from wastewater), as well as for emissions from past and present industrial and mining activities.

In general, concentrations detected during the summer flood were higher than in winter (up to mg/g TOC), likely due to additional emission sources. There was a significantly higher runoff in summer that caused more severe flooding and damage to infrastructure and urban, industrial, and agricultural areas in the entire catchment. High pollutions occurred throughout the course of the river, with the diversity of substances increasing downstream. While the upper course is predominantly natural, the lower course is characterized by urban, industrial, and agricultural land use. In addition, the largest wastewater treatment plants on the Rur itself and its tributaries are located in the lower course. Structural features such as weirs, dams, or renaturalized areas were also evident in the concentration profiles.

The findings on the importance of land use, emission sources, and structural (flood control) measures, as well as the identified dispersion profiles of various pollutant groups, provide an important basis for a comprehensive flood risk assessment.

Analysis of structurally modified polyacrylamide based flocculants by off-line thermochemolysis-GC-MS

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Polyacrylamide based flocculants are widely used in wastewater treatment and sludge dewatering processes [1]. Therefore, they are common constituents in sewage sludges, which are partly used in land applications as fertilizers and soil conditioners [2]. Although polyacrylamide and its chemical derivates are not considered as toxic compounds themselves, due to the wide usage range, direct release into the environment as well as assumed possible phytotoxic effects [3], there is a need for polyacrylamide analysis in environmental samples.

In this study, an online trimethylammonium hydroxide -thermochemolysis GC-MS analysis concept for the determination of cationic polyacrylamide (cPAA) developed by Kronimus & Schwarzbauer (2007) [3] was transferred into an off-line concept. This off-line thermochemolysis method using trimethylanilline hydroxide (TMAH) as thermochemolytic agent, induces degradation of cPAA into defined substituted glutarimide derivates as specific pyrolysis products. These pyrolysis products appeared in a typical pattern of homologues allowing an unambitious identification of the polymer as well as a pyrolysis based quantification.

Experiments were carried out on pure cPAA, spiked samples, and four sewage sludge samples from municipal wastewater treatment plants in Germany. All four specific degradation products were detected in three out of four sewage sludge samples indicating that the developed TMAH-thermochemolysis method is a viable method for cPAA detection in complex matrices and on environmentally relevant concentrations. Nevertheless, experiments on sewage sludge samples revealed cPAA contamination in a concentration range between 40 and 60 μg/g. However, for a doubtless confirmation of cPAA contamination in environmental samples, all four specific degradation products need to be validated.

1. V. S. Green, & D. E. Stott (1999), 10th International Soil Conservation Organization Meeting, West Lafayette, Indiana, (1999) 384-389.
2. M.J. Caulfield, G.C. Qiao, D.H. Solomon, Chem. Rev. 102 (2002) 3067.
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Biological markers in oil as a tool to assess the origin of oil in natural geological conditions, but also to identify and assess the fate in the environment as a polluting substance

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The analytical techniques used to determine the content and distribution of structural and stereochemical isomers of biological markers in petroleum (oil) as a fossil fuel and in petroleum as a pollutant in the environment are identical. In order to identify *n*-alkanes, isoprenoid aliphatic alkanes, polycyclic alkanes of the sterane and triterpane type, or polycyclic alkanes of the naphthalene or phenanthrene type, column chromatography methods are applied, followed by instrumental methods of gas chromatography and mass spectrometry (GC-MS, GC-MS-MS). However, the results obtained have a completely different purpose in organic geochemical investigations, and especially in the field of environmental chemistry where oil is investigated as a pollutant [1-3].

In the first case, the type of precursor biomass, deposition environment, degree of thermal maturity, length of migration path, degree of oil changes in reservoir rocks (first of all, degree of biodegradation) are evaluated based on the distribution and possibilities of the mentioned biomarkers. In environmental chemistry, biological markers serve to determine the presence of a petroleum pollutant in a sample of groundwater, surface water, sediment, or soil. They also serve to assess the extent to which the identified pollutant has been transformed by staying at the examined locality, or to the extent it has changed during migration.

If remediation procedures are performed (primarily bioremediation), biological markers are an excellent tool to evaluate the success of the performed process, regardless of whether it is performed in *ex situ* or *in situ* conditions.

This presentation will present a number of examples of the use of the mentioned biological markers in the organic geochemical examination of the assessment of the origin and geological history of oil, and on the other hand, a number of examples related to the identification of oil in the environment as a pollutant and its fate in such conditions.

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2. J. Schwarzbauer and B. Jovančićević (2018) Fundamentals in Organic Geochemistry – Organic Pollutants in the Geosphere, Heidelberg, Springer, ISBN 978-3-319-68937-1, DOI https://doi.org/10.1007/978-3-319-68938-8, 187 pp.
3. J. Schwarzbauer and B. Jovančićević (2020) Fundamentals in Organic Geochemistry – Introduction to Analytical Methods in Organic Geochemistry, Springer, Heidelberg, ISBN 978-3-030-38591-0, 128 pp.

Decarboxylation of diclofenac and formation of artefacts in the hot GC injection port

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Diclofenac is a commonly used anti-inflammatory drug and it is synthesized using an ind linone derivative [1]. Due to the thermal unstability of diclofenac, an intramolecular cyclization product (impurity A) [2] may be formed, or the oxidation of the decarboxylated diclofenac products to an alcohol (-CH_2OH, impurity C), an aldehyde (-CHO, impurity B), and other derivatives can be observed [3]. A hot GC injection port was coupled to a temperature controller; the effect of carrier gas type (air or helium), temperature (100, 150, 200, 250, and 300 °C), and preparation solvent (ethyl acetate, methanol or dichloromethane) were studied. The splitless injection mode was used, a flow rate was set at 1 mL min^{-1}, and an injection volume was 2 μL. A DB-5MS short column (0.12 m x 0.25 mm x 0.25 μm) was connected to the injection port, and the column outlet was introduced into ethyl acetate (0.5 mL); the injection lasted 1 min. Each eluate recovered in ethyl acetate was concentrated to dryness, reconstituted in water:methanol (1:1) and analyzed by UHPLC-ESI$^+$-Orbitrap-HRMS. The best analytical response obtained by LC/MS for diclofenac and its impurities A, B, C was obtained using water and methanol as mobile phase, with 0.2% (v/v) formic acid, and with the capillary voltage set at 3.5 kV. The variation coefficients were in the range of 0.04-0.2% and 0.6-4% for retention times and chromatographic areas, respectively. Minimum detection and quantification levels values were found to be between 0.2-0.9 μg L^{-1} and 0.6-3 μg L^{-1}, respectively. It was shown that in helium gas the formation of impurity A (γ-lactam) was predominant, while in the presence of air, impurities B and C were mainly formed, through a possible intermediate 2,6-dichloro-*N*-(*o*-tolyl)aniline. This study contributes to the understanding of the diclofenac thermal decomposition and the elucidation of different reaction mechanisms, which some thermolabile compounds could experiment in the hot GC injection port.

Acknowledgement

Industrial University of Santander; Chromatography and Mass Spectrometry Research Center CROM-MASS and Research Center of Excellence CENIVAM, Faculty of Science - School of Chemistry (UIS). COLCIENCIAS, Bogota, Colombia for the financial grant (No 785/2017).

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Analysis of volatile fraction of the *Cymbopogon winterianus* (Poaceae) encapsulated essential oil

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Insect-related problems can range from food damage during its storage to acquisiton of viral and other infections. Some synthetic insecticides and repellents found on the market produce high levels of resistance in the insects, pollution in ecosystems and toxic effects in people and animals [1]. It has been necessary to investigate new natural sources of compounds that have repellent effects like Cymbopogon winterianus (Poaceae) essential oil (EO), used to produce mosquito repellents [2]. However, the high volatility and instability because of temperature, humidity and light can produce damage in secondary metabolite compounds associated with insect-repellent properties. The encapsulation can be an alternative to increase the EO efficiency.

The C. winterianus essential oil was obtained by steam distillation and was encapsulated with polyethylene glycol (PEG 6000) using the melt dispersion method. Volatile compounds of the neat and encapsulated EOs were monitored by headspace solid-phase microextraction coupled to mass spectrometry (HS-SPME-GC/MS) with a fibre of poly(dimethylsiloxane)-divinylbenzene (PDMS/DVB, 65 μm). The neat EO and the encapsulated were analyzed at 0, 1,3,7 and 15 days by gas chromatography with flame-ionization detection (HS-SPMEGC/FID). The major components identified in the neat EO were geraniol (23.8%), citronellol (18.4%) and citronellal (15%). Those compounds were detected in both, free and encapsulated EO. Higher amount of monoterpene hydrocarbons was detected in the neat EO at day zero.

Oxygenated monoterpenes citronellol and geraniol in C. winterianus EO volatilized faster than those presented. Encapsulation process allowed to maintain EOs for much more time.

Aknowledegements
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Chemical composition of essential oil and extract isolated from *Hyptis colombiana* (Lamiaceae)

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Hyptis colombiana (Lamiaceae family) is a shrub native to the Colombian and Venezuelan Andes [1, 2]. The genus *Hyptis* is traditionally used for the treatment of digestive and menstrual disorders, and for respiratory diseases [3]. *Hyptis* spp. also have antimicrobial and antioxidant activities. [3]. The essential oil (EO) and extracts were obtained from *H. colombiana* plants collected in the experimental plots of CENIVAM (Bucaramanga, Colombia). The EO was analyzed and quantified by GC/MS and GC/FID. The hydroethanolic extract was analyzed a Vanquish UHPLC Ultra high-performance liquid chromatograph (Thermo Fisher Scientific, Germering, Germany), equipped with an *Orbitrap*™ mass detector (Q-Exactive, Thermo Fisher Scientific, Bremen, Germany), a heated electrospray interface (HESI-II), operated in positive or negative ion acquisition modes. The antioxidant activity of the EOs and the extracts was determined by the ORAC method. The essential oil yield was 0.08% (w/w). The major compounds identified by GC/MS were: (*E*)-β-caryophyllene (22.0%), germacrene D (14.5%), sabinene (12.5%), and caryophyllene oxide (10.2%). The chemical composition of the *H. colombiana* EO reported by Flores *et al.* [2] present similarity in the major compounds (*E*)-β-caryophyllene (29.5%), germacrene D (22.2%), caryophyllene oxide (3.5%), and bicyclogermacrene (10.9%). In the *H. colombiana* extract rosmarinic ($[M-H]^-$, *m/z* 359.22256), caffeic ($[M-H]^-$, *m/z* 179.03393) acids, and rutin ($[M-H]^-$, *m/z* 609.14546) were identified by UHPLC-ESI$^-$/*Orbitra*p-HRMS. The antioxidant activity of EO (1400 ± 36 μmol Trolox$^{®}$/g sample) and extract (4200 ± 40 μmol Trolox$^{®}$/g sample) from *H. colombiana* plants were higher than that of the reference antioxidants BHT (480 ± 14 μmol Trolox$^{®}$/g sample) and α-tocopherol (350 ± 13 μmol Trolox$^{®}$/g sample), when the ORAC assay was performed.

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GC/MS characterization of the major compounds in the essential oil and its fractions obtained by destillation of two chemotypes of *L. alba*

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Lippia alba is an aromatic species of the Verbenaceae family, it is found in shrub form, with a height of up to 1.5 m, it has oval leaves with lime, lemon or mint odor, and fruits in dupra with dark violet exocarp [1]. It is cultivated because it is a source of secondary metabolites with antiviral and antioxidantbiological activity [2]. The chemical composition of the (EO) of *L. alba* is highly variable, depending on the stage of plant development, the part used for distillation, the geographical location, the physicochemical characteristics of the soil and the climate [3]. The plant material of the two chemotypes (citral and carvone) was collected in experimental plots located in Barbosa, Santander. The EOs were obtained by steam distillation from fresh plant material. Fractionation was carried out in a distillation tower with a rotating column at reduced pressure; quantification was performed by GC-FID analysis and characterization was carried out by gas chromatography using two columns, one polar (DB-WAX) and the other apolar (DB-5MS), coupled a mass selective detector (MSD) with 70 eV ionization EI. MS in full scan acquisition mode. Linear retention indices as identification criteria, comparison of the mass spectra obtained with those reported in the Wiley, Adams and NIST databases, and confirmation with certified reference substances were used. In the *L. alba* (carvone) EO it was found, limonene (70,4%), carvone (14,8%) and germacrene (7,9%) were identified as major components; after fractionation, enrichment in piperitone (12,4%), germacrene (30,4%), carvone (27,4%) was observed. In the *L. alba* (citral) EO it was found neral (16,1%), geraniol (18,5%) and geranial (22,0%) were identified as major compo-nents, after fractionation, enrichment in limonene (39,7%), 6-methyl-5-hepten-2-one (40,2%), linalool (16,4%), caryophyllene (8,3%) was observed.

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GC/MS and LC/MS analyses of the secondary metabolites obtained by different extraction methods from *Varronia curassavica* Jacq. (Boraginaceae)

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Residual biomass derived from essential oils (EOs) distillation; is of great interest due to the bioactive compounds, remaining, in the post-distilled plant material [1]. The aim of this work was to study secondary metabolites presents in EO and extracts in *Varronia curassavica* Jacq., an aromatic shrub grown wildly in Colombia, mainly used against inflammatory diseases, gastrointestinal pain, and skin treatments [2]. The EO was obtained by microwave-assisted hydrodistillation (MWHD), and it was analyzed by GC/MS. Solvent extraction (SE), and matrix solid-phase dispersion (MSPD) were used to isolate non-volatile secondary metabolites of *V. curassavica* from fresh plants and from dried material after plant distillation. These extracts were analyzed by UHPLC-ESI-Q-Orbitrap-HRMS. The compound identification were based on chromatographic (retention times, retention indices, and standard compounds) and mass-spectral criteria (fragmentation patterns, exact masses, isotopic ratio and comparison with MS databases). Terpenoids α-pinene (180 ± 2 mg/g EO) and (*E*)-β-caryophyllene (99.0 ± 0.4 mg/g EO) were the major compounds found in the EO. The SE and MSPD extracts of the plant material obtained before its distillation showed mainly rosmarinic acid (4.40-32.0 mg/g extract) and *O*-methoxylated flavonols artemetin (8.0-16.0 mg/g extract) and hydroxy-artemetin (5.00-10.0 mg/g extract), respectively. After the distillation processes, rosmarinic acid (14.3 mg/g extract), *O*-methoxylated flavonols artemetin (15.0 mg/g extract) and hydroxy-artemetin (9.0 mg/g extract) in the hydroethanolic extract increased their concentration. The information on chemical composition of *V. curassavica* plant secondary metabolites found could be useful for pharmaceutical, cosmetic, flavor and fragrance industries.

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Comparison of the chemical composition of essential oils distilled from a wild and a domesticated *Calea spp.* (Asteraceae) plants grown in Santander, Colombia

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The genus Calea (Asteraceae) contains approximately 125 species that are distributed in the tropical and subtropical regions of America. These plants have been commonly used to treat health problems such as diabetes, hypertension, gastritis, and have been used for their anti-inflammatory, antidiarrheal, psychotropic effects, among others [1]. The objective of this work was to characterize and to compare the essential oils (EOs) obtained from wild and domesticated Calea species. The plants were collected in the surroundings of Zapatoca (Santander, Colombia). The taxonomic identification was carried out in the Herbarium at the Industrial University of Santander and the EO was obtained by steam distillation. These plants were also propagated in the CENIVAM-UIS botanical garden, located in Bucaramanga (Santander), and their EOs were obtained by hydrodistillation assisted by microwave radiation. The chemical characterization of the two EOs was carried out by gas chromatography coupled to mass spectrometry, using both polar (DB-WAX) and nonpolar (DB-5MS) columns. EO constituents were identified by comparing of their mass spectra (EI, 70 eV) with those from spectral databases (ADAMS, NIST, Wiley), by comparing of their linear retention indices with those reported in the literature [2] and by using also of some standard compounds. The EOs distilled from the domesticated and the wild plants were rich in terpenic hidrocarbons (47,4 % and 55,8 %, respectively), the main compounds were germacrene D, α-pinene and α-thujene. The EO distilled from domesticated and wild plants showed notable differences in germacrene D amount (17,6 % and 4,3 %, respectively) and α-pinene amount (9,0 % and 20,8 %, respectively). However, these two plants presented similar major compounds, namely, α-thujene (15,7 % and 23,5 %, respectively), sabinene (4,0 % and 3,5 %, respectively), and β-myrcene (7,4 % and 3,6 %, respectively). This study showed that the composition of the Calea spp. EOs can vary with the process of the plant domestication.

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Determination by UHPLC/ESI-Orbitrap-MS of anti-inflammatory compounds and their metabolites after interaction with *Salvinia adnata* Desv. in aqueous medium

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In Colombia, the most frequently consumed drugs are non-steroidal anti-inflammatory medecines (NSAIDs). Some of these compounds can enter to the environment through wastewater treatment effluents [1], which transport them to supply sources, that are used for consumption and irrigation of agricultural crops [2]. The recovery of diclofenac, ibuprofen, naproxen, and piroxicam compounds added to aqueous matrices was carried out using the solid phase extraction technique (SPE), with extraction efficiency between 94-99% for the Strata X® cartridge (100 mg); their analysis was carried out by HPLC/DAD. The analysis by UHPLC/ESI-Orbitrap-MS was performed following the implementation of the extraction methodology for the compounds in water samples with the aquatic plant Salvinia adnata Desv presented. The best analytical response was obtained using water and methanol as mobile phase with 0.1% v/v formic acid and 5 mM ammonium formate; an ESI interface capillary voltage was set at ± 3.5 kV. Hydroxylated and conjugated NSAID metabolites were the main compounds identified in the extracts. The developed study could be useful to monitor the process of absorption and elimination of metabolites in polluted waters, in the presence of aquatic plants.

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LC/MS study of ergoline alkaloids isolated from *Ipomoea tricolor* (Convolvulaceae) seeds

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Ipomoea tricolor (Convolvulaceae) seeds contain ergoline alkaloids derived from indole, such as ergine (LSA), ergometrine, ergometrinine, among others [1]. Some of them are well-known for their psychotropic effects and for generating of the ergotism condition. Ergolinic alkaloids have been used as precursors for the synthesis of various compounds, used for the treatment of Parkinson's disease, vasoconstriction, etc [2].

I. tricolor seeds (1 g) collected from CENIVAM-UIS research experimental plots (Bucaramanga, Colombia) was used to obtain the extracts. The matrix solid-phase dispersion technique (MSPD) with modified C_{18} silica gel as adsorbent and acetone as an elution solvent was the method used for extract obtaining. The extracts were analyzed by UHPLC-ESI/*Orbitrap*-MS, the ion-products were formed from $[M+H]^+$ at 10, 20, 30, 40 eV, in the higher-energy collision cell (HCD). For compound identification the following criteria were employed: (1) determination of the exact masses of the protonated molecule, and their elemental composition,; (2) the study of the fragmentation pattern; (3) the study of the isotopic distribution, and (4) the comparison of the mass spectra with those reported in the literature.

The extraction yield obtained was 3.0 %, two ergoline alkaloids were isolated from *I. tricolor*, *i.e.*, ergine $C_{16}H_{17}N_3O$ $[(M+H)^+$, *m/z* 268.14392] and ergometrine $C_{19}H_{23}N_3O_2$ $[(M+H)^+$, *m/z* 326.18467]. Characteristic producto-ions were registered at *m/z* 223.12262 $[(M+H)\text{-}CONH_2]^+$ corresponding to the alpha cleavage of the amide group, and at *m/z* 251.11737 $[(M+H)\text{-}NH_2]^+$, resulting from the loss of the amino group in ergine. *I. tricolor* seeds can be a valuable source of ergoline alkaloids, used as a starting material for the synthesis of various new drugs and bioproducts.

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Determination by UHPLC/ESI(+)-Orbitrap of cocaine in caterpillar after coca fruit eating

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Plants and insects have coexisted for at least 350 million years. In that period, they involved a variety of different evolutive interactions [1]. To prevent the herbivore attack, plants produce proteins and secondary metabolites that have physiological effects on the herbivores [2]. However, these interactions are very complex and the functions that many of these compounds perform are still unknown. In the case of *Erythroxylum novogranatense* (coca), insects as butterflies, bees and caterpillars, can frequently interact with the plant during its flowering phase. The principal alkaloid in coca leaves, flowers and fruits is cocaine (COC), a psychostimulant that metabolized to benzoylecgonine (BE), ecgonine methyl ester (EME) and ecgonine (ECG), by different metabolic pathways [3].

In this research work, COC, BE and cinnamoylcocaines (CIN) were isolated by matrix-solid phase dispersion (MSPD) extraction in caterpillar after coca fruit eating. The target analytes were identified using their exact masses, the isotopic relation and the fragmentation patterns, registered by Orbitrap-MS. The fragmentation patterns were obtained at different HCD cell energies (10, 20, 30, and 40 eV).

The major LC peaks areas in the extracted ion chromatograms (EIC) of $[M+H]^+$ at *m/z* 304.15433 (COC), *m/z* 290.13868 (BE), and *m/z* 330.16998 (CIN) were obtained at Full MS and using 10 eV HCD energy. The mass defect for all ions detected don't exceed 2 ppm. BE was the principal alkaloid detected in caterpillar extract. Other alkaloids commonly found in coca, *e.g.*, methylecgonine, tropacocaine, and truxillines were not identified. These results provide new information about the interaction coca-insect and generate questions about how the caterpillar metabolizes the alkaloids present in the coca fruit.

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Chemical composition studied by GC/MS and GC/FID of *Cymbopogon winterianus* essential oils from Colombia

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Citronella Java Type (*C. winterianus*) are grasses that grow more than 1 m tall. The grasses are harvested two to three times a year and have characteristic rose and lemon scents [1]. *C. winterianus* (Poaceae) is a highly demanded aromatic crop grown in several countries and used as a fragrance, insect repellent and in Asian cuisine [2]. The citronella Java Type oil contains high concentrations of citronellol (35%) and geraniol (21%) [1]. it differs from *C. nardus* because the geraniol content is higher (25-40%) than citronellal (5-15%) [3]. In this study, leaves of *C. winterianus* were collected at the Barbosa UIS campus (Santander, Colombia). The essential oils were obtained by steam distillation. The samples were sent to the CENIVAM (Bucaramanga, Colombia) to determine the chemical composition by GC/MS and GC/FID. The identification of the compounds present in the essential oils was performed by GC/MS, on GC 6890 Plus gas chromatogram (Agilent Technologies, AT, Palo Alto, CA, USA), equipped with a mass selective detector MS 5973 Network (AT, Palo Alto, CA, USA), using a DB-5MS column [5%-phenyl-poly-(methylsiloxane), 60 m x 0.25mm d.i x 0.25 d_f)] and a DB-WAX [poly-(ethylene glycol), 60 m x 0.25 mm d.i x 0.25 d_f]. The quantification was done by the GC/FID. In the *C. winterianus* essential oils, limonene (1.7-3.0%), citronellal (37.2-46.9%), citronellol (16.5-26.5%), geraniol (12.2-23.3%), citronellyl acetate (0.8-2.6%), and elemol (1.1-1.7%) were identified as major components. Comparing the results obtained with those reported according to the international standard ISO (3848:2016) [4], citronellal (31.0 -40.0%), citronellol (8.5 -14.0) and geraniol (20.0 – 25.0), the essential oils of citronella planted in the Santander rural farms (Colombia) have a high quality and can be commercialized as raw material to the pharmaceutical, food or cosmetic industries.

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Chemical characterization by UHPLC-ESI/*Orbitrap*-MS of the extracts obtained from *Ocimum campechianum*

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Ocimum campechianum, known as clove basil, is an aromatic herb of the Lamiaceae family. Few studies have been reported on the chemical composition of the extracts obtained from this plant species. According to Tachinni *et al*., rosmarinic acid is a main compound present in *O. campechianum* [1].

O. campechianum dry and distilled aerial parts of were used to obtain the extracts by matrix solid-phase dispersion (MSPD) and hydroethanolic extraction. Chemical identification of secondary metabolites was performed by UHPLC-ESI/*Orbitrap*-MS [2]. The exact masses of the protonated and deprotonated molecules were determined in the positive and negative ion acquisition modes. The chemical characterization was performed by comparing the characteristic ion-products, identified in the analysis of the extracts isolated from *O. campechianum* and using the reference substances for the identification of compounds.

EtOH/H_2O extracts were obtained with a yield of 8.9% using dry material and 5.3% with plant material after distillation; for MSPD extracts, 11.4% and 6.3% were the extraction yields obtained from dry plant material and after its distillation, respectively. In all extracts, it was rosmarinic and ursolic acids, rutin, luteolin, and apigenin were found. The major secondary metabolite identified in all *O. campechianum* extracts was rosmarinic acid the higher relative amount was found in the MSPD extracts isolated from plant material after its distillation.

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Chemical composition of essential oils and extracts isolated from plants of the genus *Cymbopogon*, cultivated in Colombia

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The species of the *Cymbopogon* genus are source of compounds of pharmacological interest, because their secondary metabolites showed anti-inflammatory, antifungal, antibacterial, and anthelmintic activities [1]. Citronella Java type (*C. winterianus*) and palmarrosa (*C. martinii*) are aromatic plants which belong to the Poaceae family, and are known for their essential oils, rich in geraniol, citronellol and citronellal [2]. *C. winterianus* and *C. martinii* plants were collected in the experimental plots of CENIVAM (Bucaramanga, Colombia). Essential oils (EOs) were obtained by steam distillation (SD) and their chemical characterization and quantification were performed by GC/MS and GC/FID. The extracts, which were obtained by hydroalcoholic mixture, were analyzed by HPLC/DAD and UHPLC-ESI/*Orbitrap* on a Dionex Ultimate 3000 chromatograph (UHPLC, Thermo Scientific, Sunnyvale, CA, USA) operated in negative or positive ion acquisition modes. The antioxidant activity of extracts was evaluated by ORAC and ABTS$^{+\bullet}$ methods. In the *C. martinii* EO, geraniol 84.1% (900 ± 147 mg/g EO), geranyl acetate 8.1% (50 ± 23 mg/g EO) and linalool 2.3% (30 ± 5 mg/g EO) were main compounds. In the *C. winterianus* EO, citronellal 41.1% (400 ± 77 mg/g EO), geraniol 16.8% (160 ± 23 mg/g EO) and citronellol 15.7% (140 ± 9 mg/g EO) were identified as principal compounds. In the *C. martinii* and *C. winterianus* extracts, chlorogenic [M-H]$^-$ *m/z* 353.08743, caffeic [M-H]$^-$ *m/z* 179.03396, *p*-coumaric [M-H]$^-$ *m/z* 163.03896, ferulic [M-H]$^-$ *m/z* 193.04971, *p*-hydroxybenzoic [M-H]$^-$ *m/z* 137.02353, and 4-caffeoylquinic [M-H]$^-$ *m/z* 353.08789 acids, and flavones apigenin-8-*C*-glucoside and apigenin-*C*-hexoside [M+H]$^+$ *m/z* 433.11255, luteolin-*C*-hexoside [M+H]$^+$ *m/z* 449.10696, luteolin-*C*-hexoside-*C*-pentoside [M+H]$^+$ *m/z* 581.14978, apigenin-*C,C*-dihexoside, luteolin-*O*-desoxyhexosyl-*C*-pentoside, and luteolin-*O*-rutinoside [M+H]$^+$ *m/z* 595.16571, were detected. The values of µmol Trolox®/g extract, of the *C. winterianus* extract, evaluated by the ORAC method (1650 ± 70) was higher than that found for the *C. martinii* extract (1500 ± 249), while the antioxidant activities evaluated by the ABTS$^{+\bullet}$ method were similar for both extracts (100 ± 35 µmol Trolox®/g extract and 80 ± 2 µmol Trolox®/g extract, respectively). The extracts obtained from the residual material after plant distillation were rich in *C*-glycosyl flavones and phenolic acids.

Acknowledgement

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Fractional distillation at reduced pressure of orange essential oils and their respective prins reaction product, homolimonenol

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Citrus sinensis (orange) is a plant of the citrus family native to Southeast Asia. From the orange peel and by steam distillation its essential oil can be obtained [1]. Orange essential oil (EO), rich in limonene, showed a dissuasive effect on the oviposition of Drosophila suzukii or fruit fly [2]. The catalytic transformation of limonene to homolimonenol using the Prins reaction, a higher-value homoallylic alcohol, was reported to valorize agro-industrial waste [3]. In the present work the major components of orange EO were enriched and its respective homolimonenol reaction product was obtained by fractional distillation at reduced pressure. The chemical characterization of EO and its respective reaction product was performed by GC/MS. An apolar DB-5MS and a polar DB-WAX columns were used, both 60 m, split injection 1:30, MSD (EI, 70 eV). The compound identification was made based on the linear retention indices and by comparing of experimental spectra with those from the spectral databases (Adams, Nist, Wiley). Confirmatory identification of the main component was performed using reference substances. Limonene from EO (92%) was enriched to 95% in a rotary-shaft fractionation column, the value was higher than the concentration achieved by Singh et al. in a packed column [4]. Homolimonenol (43%), the oxygenated component of the EO transformed, was enriched up to 73%. In this work, homoallylic alcohol was concentrated at the top fraction of the fractionation process, this technique is generally used for the EO deterpenation. The results indicate that EO fractionation in a rotary axis column may be more effective than fractionation in packed columns.

Acknowledgment
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Oil fingerprinting for unconventional reservoir samples using GC×GC-TOFMS, FT ICRMS and EA-IRMS

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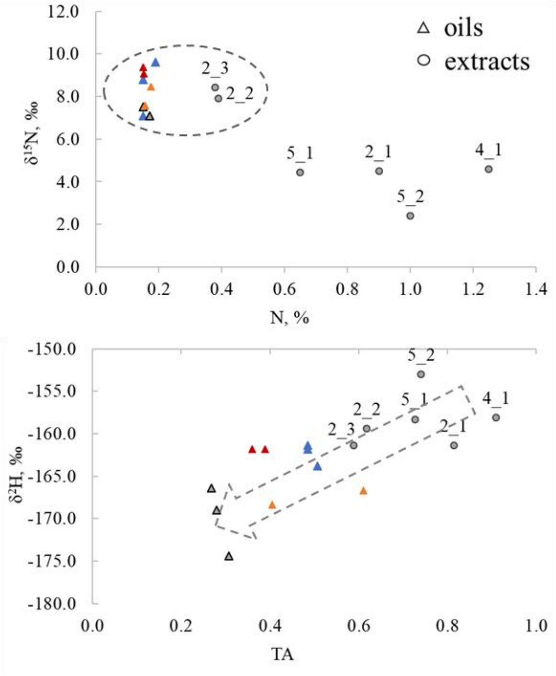
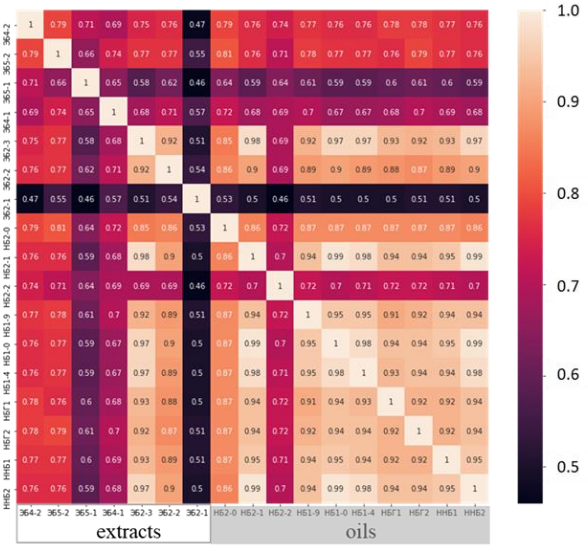
The presentation considers the variations in composition of oils and rock extracts analyzed using three analytical methods: GC×GC-TOFMS, ESI FT-ICR MS and EA-IRMS. The differences in elemental, isotope and molecular composition of samples result from petroleum generation and migration processes in unconventional reservoir, as well as production technologies applied. The aim was to perform oil fingerprinting and to find the features of oil composition, reflecting each of the above mentioned processes based on the oil collection from one oilfield of the Bazhenov Formation, West Siberia Petroleum Basin.





	364-2	365-2	365-1	364-1	362-3	362-2	362-1	НБ2-0	НБ2-1	НБ2-2	НБ1-9	НБ1-0	НБ1-4	НБГ1	НБГ2	ННБ1	ННБ2
364-2	1	0.79	0.71	0.69	0.75	0.76	0.47	0.79	0.76	0.74	0.77	0.76	0.76	0.78	0.78	0.77	0.76
365-2	0.79	1	0.66	0.74	0.77	0.77	0.55	0.81	0.76	0.71	0.78	0.77	0.77	0.76	0.79	0.77	0.76
365-1	0.71	0.66	1	0.65	0.58	0.62	0.46	0.64	0.59	0.64	0.61	0.59	0.59	0.6	0.61	0.6	0.59
364-1	0.69	0.74	0.65	1	0.68	0.71	0.57	0.72	0.68	0.69	0.7	0.67	0.67	0.68	0.7	0.69	0.68
362-3	0.75	0.77	0.58	0.68	1	0.92	0.51	0.85	0.98	0.69	0.92	0.97	0.97	0.93	0.92	0.93	0.97
362-2	0.76	0.77	0.62	0.71	0.92	1	0.54	0.86	0.9	0.69	0.89	0.9	0.89	0.88	0.87	0.89	0.9
362-1	0.47	0.55	0.46	0.57	0.51	0.54	1	0.53	0.5	0.46	0.51	0.5	0.5	0.5	0.51	0.51	0.5
НБ2-0	0.79	0.81	0.64	0.72	0.85	0.86	0.53	1	0.86	0.72	0.87	0.87	0.87	0.87	0.87	0.87	0.86
НБ2-1	0.76	0.76	0.59	0.68	0.98	0.9	0.5	0.86	1	0.7	0.94	0.99	0.98	0.94	0.94	0.95	0.99
НБ2-2	0.74	0.71	0.64	0.69	0.69	0.69	0.46	0.72	0.7	1	0.72	0.7	0.71	0.72	0.72	0.71	0.7
НБ1-9	0.77	0.78	0.61	0.7	0.92	0.89	0.51	0.87	0.94	0.72	1	0.95	0.95	0.91	0.92	0.94	0.94
НБ1-0	0.76	0.77	0.59	0.67	0.97	0.9	0.5	0.87	0.99	0.7	0.95	1	0.98	0.94	0.94	0.95	0.99
НБ1-4	0.76	0.77	0.59	0.67	0.97	0.89	0.5	0.87	0.98	0.71	0.95	0.98	1	0.93	0.94	0.94	0.98
НБГ1	0.78	0.76	0.6	0.68	0.93	0.88	0.5	0.87	0.94	0.72	0.91	0.94	0.93	1	0.92	0.92	0.94
НБГ2	0.78	0.79	0.61	0.7	0.92	0.87	0.51	0.87	0.94	0.72	0.92	0.94	0.94	0.92	1	0.92	0.94
ННБ1	0.77	0.77	0.6	0.69	0.93	0.89	0.51	0.87	0.95	0.71	0.94	0.95	0.94	0.92	0.92	1	0.95
ННБ2	0.76	0.76	0.59	0.68	0.97	0.9	0.5	0.86	0.99	0.7	0.94	0.99	0.98	0.94	0.94	0.95	1
	extracts							oils									

The study reveals, that accumulating intervals (between the Lower and the Upper Bazhenov) contribute to the oil from all the studied wells, rock extracts from this interval are characterized by lower maturity according to TA, 4/1-MDBT and $\delta^{13}C$. The migration of hydrocarbons from source rocks to accumulating rocks is associated with the loss of nitrogen and depletion of ^{15}N, the oils and productive intervals could be correlated by close values of $\delta^{15}N$. The similarity of the samples is confirmed by a comparison of polar components composition obtained by FTICRMS.

The collection includes oil samples before and after thermal treatment of the reservoir, they differ in $\delta^{2}H$ whereas biomarker parameters indicate an increase in the percent of the hydrocarbons from accumulating intervals.

The obtained results form a fundamental background for oil production monitoring from unconventional heterogeneous reservoirs.

Reconstruction of organic matter accumulation conditions derived from elemental, molecular and isotope composition of rocks

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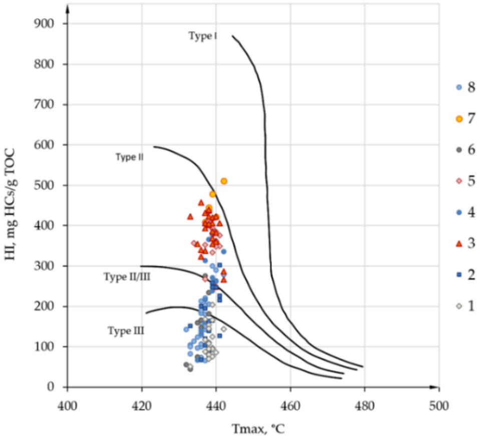

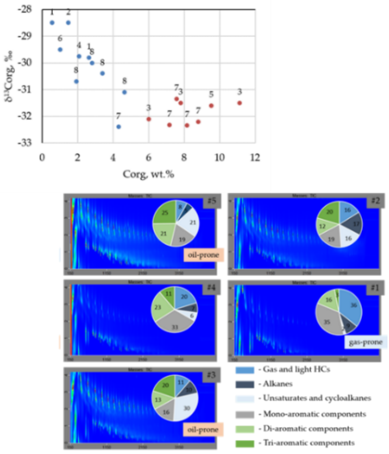

The study is devoted to the reconstruction of organic matter accumulation conditions in the Upper Jurassic-Lower Cretaceous period in one of the least studied areas of the West Siberian sedimentary basin – it's northern part [1]. The reconstruction is based on the results of analyses of unconventional reservoir rocks containing up to 15 wt.% of organic matter. Genesis of the mineral part of the rock was revealed from analyses of macro- and micro-elements composition and their ratios as proxies for sedimentation conditions (Al, U, Mo, Mn, and others), and isotope studies (δ^{13}Corg, δ^{15}N, δ^{34}S). Organic matter pyrolysis studies, molecular, isotope (δ^{13}C, δ^{15}N, δ^{34}S), and biomarker composition analyses including pyro-GC×GC-TOFMS of kerogen were performed. The results were integrated into the sedimentation model.

It has been shown that the accumulation of organic matter (TOC) was mainly controlled by the redox conditions and terrigenous material influx during sedimentation in the studied area. A simultaneous change in the redox conditions and the amount of terrigenous material is associated with eustatic sea level fluctuations. Periods of sea level transgression are associated with reducing conditions and intensive accumulation of marine organic matter at low rates, such environments were periodically interrupted by oxidative environments with a more pronounced influx of terrigenous material. Under oxygen conditions with an increased proportion of terrigenous material, depleted in organic matter rocks were formed, which contain gas-generating kerogen in contrast to oil-bearing rocks typical for the central part of the Bazhenov Formation. As the result, the deposits are characterized by variations of the content and composition of organic matter.

To sum up, we have reconstructed the paleo sedimentation conditions for the deposits in the northern part of West Siberia using an integrated geochemical approach. The relationship between composition of source rocks and their petroleum generation properties were evaluated.

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Doxazosin degradation with gamma irradiation

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Pharmaceuticals and pharmaceutical active substances used in human and veterinary medicine (such as painkillers, antibiotics, hormones, anti-inflammatory drugs, lipid regulators, beta blockers, anti-cancer drugs) and as personal care products represent the group of new pollutants, so called emerging pollutants. Their continuous release to the environment as complex mixtures can result in higher concentrations, long-term and negative effects on aquatic and terrestrial organisms. For these reasons various methods for removal of pharmaceuticals from aqueous compartments have been developed.

Doxazosin, a selective alpha blocker, is widely used in medical therapy as an effective antihypertensive agent. It is very frequently prescribed drug and for this reason, environmental and ecotoxicological research is of great importance in terms of exposure and risk for both aquatic species and humans. In this study we focused on degradation of doxazosin with gamma irradiation, with the emphasis on identification of degradation products.

The experiments were performed in a panoramic type 60Co-γ irradiation chamber at Ruđer Bošković Institute (Zagreb, Croatia). The applied dose rates were 0.65 Gy/s and 6,9 Gy/s. Dose mapping of the irradiation facility has been performed experimentally (using ionizing chambers and ECB dosimetric system) and by simulation calculations. Doxazosin aqueous solutions were irradiated with 100 and 200 Gy in equilibrium with the air and the temperature was kept constant during the irradiation process at 20 ± 2 °C.

Selected samples have been further concentrated for analysis. LC-MS/MS was conducted using a high-resolution quadrupole-time-of-flight mass spectrometer TripleTOF 5600+ (Sciex, Canada). The separation of products was achieved by reversed phase liquid chromatography in a gradient elution mode. Ionization was carried out in the positive electrospray mode with further detection by Information Dependent Acquisition (IDA) scanning. This approach allowed observing the formation of several major degradation products depending on the dosage. Based on the exact masses, isotopic distribution, fragmentation pathways, and elemental compositions of the ions in the mass spectrum, the transformation products were identified. Among them, C22H21N5O8 (demethylation and oxidation), C17H23N5O5 and C17H23N5O6 (cleavage of the dioxane cycle), C23H25N5O6 (hydroxylation), and C15H21N5O5 (cleavage of both dioxane and piperidine cycle) are dominated. The detailed degradation pathway has been proposed.

Rana temporaria: de novo sequencing of Arkhangelsk population skin peptides and comparison of four populations

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Skin secretion released by amphibians during stress is a complex mixture of peptides with broad activities spectrum: antimicrobial, antifungal, antitumor, etc. These peptides are interesting object of study as models for novel pharmaceuticals, but sequencing of these molecules is a difficult task, especially for disulfide bond containing peptides such as Brevinins 1 and 2, Ranatuerins, etc.

Nowadays mass spectrometry become the most popular sequencing technique. In this work manual *de novo* sequencing of peptides from skin secretion of *Rana temporaria* from Arkhangelsk region was performed. *Rana temporaria* is a widely distributed in Eurasia frog specie, so there was a possibility to compare established peptidome with previously studied peptidomes of Italian [1,2], Moscow [3] and Central Slovenian [4] populations, using 2D mass mapping.

Experiments were carried out on Orbitrap Fusion mass spectrometer with Easy nano-LC 1000. CID, HCD and EThcD spectra were used for manual *de novo* sequencing. In total 33 peptides were discovered in this sample, including 4 novel temporins and Brevinin 2Td, predicted by cDNA cloning, but firstly observed in skin secretion.

We used EThcD fragmentation to differentiate isomeric Leu/Ile residues in sequences. It was showed that MS^3 experiment may be pretty helpful for disulfide bond containing peptides. Using complementary HCD and EThcD spectra allowed us to clarify amino acid sequences inside «Rana box».

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Revealing the urban environmental pollution through snow analysis

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Environmental exposure assessment is an important step in establishing a list of local priority pollutants and finding the sources of the threats. 2 big cities in the North-European and central parts of Russia – Arkhangelsk and Moscow were chosen as objects of study. Environment of these cities is significantly influenced by a number of industrial facilities and active car traffic. Arkhangelsk experiences subarctic climate with heavy snowfalls during 7 months, while Moscow city has a more moderate continental climate with winter period almost up to 6 months. Therefore, snow analysis represents an efficient approach for the estimation of long-term air pollution during winter period due to accumulation and preservation of environmental contaminants by snow.

Snow samples were collected during several studies in 2018-2021 in Arkhangelsk and Moscow. Classical liquid-liquid extraction of molten water with dichloromethane was used for sample preparation. The extracts were analyzed using Pegasus GC-HRT+ 4D high-resolution mass spectrometer combined with Agilent 7890A gas chromatograph in both single GC and GC×GC mode. Identification and quantification of priority pollutants was done using standards, while NIST20 mass spectral library together with manual structural elucidation were used for identification of unexpected or unknown compounds. Quantification of some other environmentally relevant compounds, for which the standards were missing, was carried out considering the response factors being equal to 1.

In addition to the classic priority pollutants listed by the US EPA (polycyclic aromatic hydrocarbons, phenols, phthalates, etc.), non-target analysis allowed identifying a wide range of organic compounds, including alkyl pyridines, organophosphates, furans, organic acids, etc. High resolution mass spectrometry was the key analytical tool during identification of unknown compounds, while addition of complementary ionization methods simplified identification.

These methods also significantly increased sensitivity towards several classes of compounds (for example nitro-compounds or polyhalogenated derivatives). Some of them haven't been identified in environmental samples for a long time ago, i.e. persistent organic pollutants (POP) from the "Dirty dozen". Finally, the large data array was processed with various chemometric approaches (ChromaTOF Tile, MetaboAnalyst and open-source software protocols) to reveal any consistent patterns for distribution of pollutants helping to find the possible sources of air pollution.

Acknowledgements
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Screening and determination of nitrogen-containing organic compounds in snow by thermal desorption gas chromatography - high resolution mass spectrometry with stir based sorptive extraction

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Nitrogen-containing organic pollutants are increasingly detected in the study of atmospheric air and snow cover in the Arctic. These include both known priority pollutants (for example, pyridine) and new (emergent) compounds released into the atmosphere as a result of human activities in the region or global circulation of air masses.

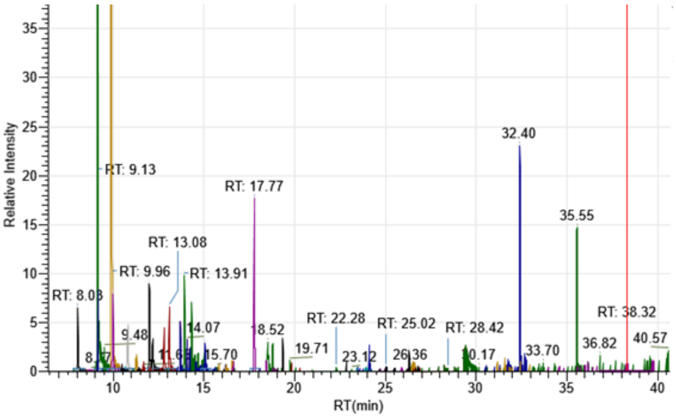

Figure - TD-GC-HRMS chromatogram of a snow sample in the SIM of nitrogen-containing compounds.

The most effective method for searching, identifying and determining a wide range of nitrogen-containing compounds in snow is gas chromatography - high-resolution mass spectrometry (GC-HRMS), however, the key problem of its application is sample preparation, which ensures efficient extraction and concentration of analytes contained in trace concentrations. To solve this problem, we have proposed the use of stir bar sorptive extraction (SBSE), implemented using a magnetic stirrer with a sorption coating. 35 compounds of various classes were used as test analytes, mainly heterocyclic compounds: pyridine, pyrrole, pyrazole, imidazole, indole, and their methyl derivatives. Comparison the efficiency of sorption coatings based on polyethylene glycol (PEG) and polydimethylsiloxane (PDMS) showed that PDMS coatings have an advantage and make it possible to achieve high recovery rates of analytes. The optimization of extraction and thermal desorption conditions was carried out. The combination of stir bar sorptive extraction for 1 hour from a 0.5 L aqueous sample with direct thermal desorption of concentrated analytes and GC-HRMS analysis achieved detection limits of tens of ng/L. This method of sample preparation makes it possible to avoid contamination of the studied samples, which is inherent in traditional methods of liquid-liquid extraction with the evaporation of large volumes of the solvent.

The developed approach has been successfully tested in the study of snow samples taken in the Arkhangelsk region. As the main nitrogen-containing pollutants in the snow samples, pyridine and its derivatives (2-methylpyridine, 2,4-dimethylpyridine, 2,4,6-trimethylpyridine, etc.), pyrol and its derivatives (N-methylpyrol, 2,5-dimethylpyrol), pyrazine, as well as 2-cyanopyridine was found.

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Thermal desorption gas chromatography – mass spectrometry determination and screening of toxic rocket fuel transformation products in sandy soils

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The use of gas chromatography - mass spectrometry methods to determine the transformation products of highly toxic rocket fuel based on 1,1-dimethylhydrazine (UDMH) in contaminated soils (near carrier rocket launch pads and at spent stages landing sites) requires solving the problems of matrix change and concentration analytes. For this purpose, methods of liquid extraction are used, as well as solid-phase microextraction from an equilibrium vapor phase, which are characterized by high labor intensity, high consumption of the extractant (liquid extraction) and significant matrix effects (SPME).

This study proposes an alternative approach to screening and simultaneous determination of a wide range of nitrogen-containing products of UDMH oxidation, based on direct thermal desorption of analytes from soil with cryofocusing and further gas chromatography-mass spectrometry analysis.

The effect of thermal desorption conditions (temperature, duration, sample weight and humidity) on the extraction efficiency and stability of analytes for the four types of soils (sandy, light, medium, and heavy loam) was studied. On this basis, the optimal parameters for the extraction of analytes were proposed: thermal desorption of a 5 mg sample at a temperature of 300 °C for sandy soil for 30 min. The achieved analyte recoveries were in the range of 30–100%. It is shown that when cryofocusing is applied, the limiting moisture content of the soil sample should not exceed 10% to maintain effective chromatographic separation. The use of sorption traps for analytes instead of cryofocusing makes it possible to analyze soils with a moisture content of up to 20%.

The use of an isotopically labelled internal standard (pyridine-d5) allowed increasing the reproducibility and accuracy of the analysis and developing a method for the simultaneous determination of 15 nitrogen-containing compounds of various classes in sandy soils with detection limits for most analytes in the range of 0.2-8 μg/kg and accuracy 80-100%. The developed method was tested in the analysis of real samples - sandy soil samples taken from the site of accidental crash of the Proton-M carrier rocket near the Baikonur cosmodrome in 2013. Most of the target analytes were found at the levels of 0.06-800 mg/kg. High accuracy of the developed sample preparation technique was confirmed by comparing the analysis results with that obtained by independent method of pressurized liquid extraction with acetonitrile.

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Derivatization of small peptides for their analysis by ESI and MALDI high resolution mass spectrometry

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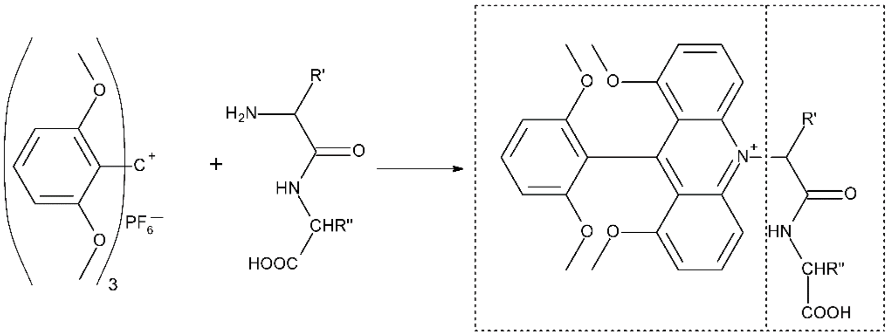
One of the important areas in rapidly developing science in structural biology, known as metabolomics, is associated with the analysis of low molecular weight peptides in the metabolome in the process of elucidating their origin and role in the existence of a living organism [1]. In principle, a complex of studies in the field of detection of peptides and their interactions with other components of the metabolome is classified as peptidomics, which constitutes an independent sub-branch of the vast science proteomics. Small peptides that make up the peptidome are present in the metabolome together with amino acids, and all these components are predominantly formed during a protein hydrolysis. Sometimes the peptidome may contain dipeptides of exogenous nature, which appears in the body due to the introduced drugs. One of the most sensitive and express approaches for studying the metabolome and, in particular, the peptidome is mass spectrometry (MS) based on various ionization methods, which is usually used in combination with separation techniques. However, when detecting native small peptides, these techniques encounter some problems. The most of them are due to the fact that the detection and quantification of targeted dipeptides is difficult against the interfering matrix and background signals in noisy low molecular weight regions of mass spectra. One of the common approaches aimed at eliminating these shortcomings, is based on the use of chemical modification (derivatization). In our work, we describe a new approach for detection of small peptides using their derivatization by tris(2,6-dimethoxyphenyl)methilium hexafluorophosphate (TDPMH) yielding fixed-charged derivatives:



TDPMH **Dipeptide** **Q$^+$** **Dipeptide**

$[Cat]^+ = Q^+$ - dipeptide

ESI and MALDI mass spectra of dipeptides derivatized with TDPMH are rather simple and usually reveal peaks of the expected heaviest ions [Cat]+ which were indicated in Scheme as [Q+dipeptide]. The comparison of LODs for initial and derivatized peptides LOD shows that the latter values are two or more orders lower than the values obtained for non-modified dipeptides allowing to detect small peptides in ultra-low qunatities.

Russian Arctic environmental studies using mass spectrometry

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Arctic environment is highly sensitive. Nowadays several international databases contain valuable information on the priority and emerging contaminants in various Arctic regions. Nevertheless, Russian Arctic may be called “terra incognita”. There is few data dealing with the environmental situation in the Russian Arctic. The present study deals with organic contaminants in the air, snow, soil, and water samples from the Franz Joseph Land, Novaya Zemlya archipelago, all the seas of the Russian Arctic, and Arkhangelsk.

Air samples were collected from 16 sites along the Russian Arctic coast from the White Sea to the East Siberian Sea. The snow samples were collected within the expeditions of “Prof. Molchanov” ship in 2017 - 2022. The analyses were done according to US EPA 8260 and 8270 method using GC-HRMS and GC×GC-HRMS with EI, CI in positive and negative ion mode with modified Pegasus® GC-HRT+4D instrument (LECO, USA). NIST20 library and manual spectra elucidation was used for the identification. LC-HRMS instruments orbitrap Q-Exactive Plus (Thermo scientific, USA) and TripleTOF 5600+ (ABSciex, Canada) were used for the identification of 1,1-dimethylhydrazine (UDMH) transformation products in soil and disinfection by-products in tap and pool water samples.

Although air quality was supposed to be rather high over 80 priority pollutants were detected in the samples collected in the Nothern seas of the Russian Arctic. Moreover, the levels of some pollutants, like phenol, were 60% of the safe levels of the continental Russia. Various hydrocarbons, phthalates, fatty acids, terpenes were the main organic compounds in the snow samples. Only several priority pollutants were identified (phenol, pyridine, phthalates, PAH). High levels of fatty acids and CxHyOz compounds with DBE 0 may occur due to intensive photo-oxidation processes involving saturated hydrocarbons in the atmosphere or on the snow surface. Persistent organic pollutants (POP) like chlorinated hydrocarbons, pesticides, etc., which are usually used as environmental indicators, were poorly presented only by several phosphates, i.e. tri(2-chloroethyl) phosphate. Fatty amides worth special mentioning. Their origin may involve humic matter or some anthropogenic sources. The derivatives of fatty amides were reliably identified among disinfection by-products in the Arkhangelsk tap water.

Special interest represents pyridine. Laboratory experiments related its origin to peat fires.UDMH is the most common rocket fuel used in the launched from cosmodrome Plesetsk in Russian North. Being highly reactive, 1,1-dimethylhydrazine easily undergoes oxidative transformation with the formation of a number of hazardous compounds causing damage to vulnerable arctic ecosystems. HRMS used to study the reactions of UDMH oxidations allowed identifying hundreds of novel nitrogen-containing transformation products of CHN and CHNO classes, formed via radical processes. Spatial distribution and migration of the major UDMH transformation products in the peaty soils of rocket stage fall place was studied.

The obtained results represent unique information on the organic pollutants in Arctic environment obtained by reliable chromatography HRMS non-target analysis.

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Novel derivatization approach for detection of sulfur compounds in crude oil

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Polycyclic aromatic sulfur-containing compounds are widely distributed in oil, especially in its low-volatile and heavy fractions (resins, asphaltenes), and this dictates the need for their determination when reliable methods for sulfur removing, cleaning and processing oil are developed. In these cases, “soft” ionization mass spectrometry methods, based on electrospray ionization (ESI) and matrix-assisted laser desorption / ionization (MALDI), are particularly effective. However, aromatic sulfur-containing compounds possess low polarity and cannot be readily ionized by these methods. To overcome the problem, their preliminary conversion into sulfonium salts by the action of alkyl iodides and silver-containing agent is widely used. In our work, we propose a new derivatization approach based on alkylation of sulfur compounds by alcohols in presence of triflic acid.

Dibenzothiophene, 4-methyl, 4,6-dimethyl and 4,6-diethyl substituted dibenzothiophenes, thianthrene and dibenzyl sulfide were used as model compounds for reaction conditions optimization, triflic acid and fatty alcohols from ethanol to octadecanol were used for derivatization. The developed approach was tested using crude oil from Romashkinskoye oilfield. Derivatization was performed by adding of 20 µl of an alcohol to solution of crude oil or model compounds in benzene, followed by addition of 20 µl of triflic acid. The mixture was hold on a vortex mixer for 40 min at 80°C. A sign of the reaction was the turbidity of the solution and the formation of drops of an isolated colored liquid at the vial bottom. The reaction mixture was cooled to room temperature and 300 µl of glacial acetic acid was added, thoroughly mixed and centrifuged at 6000 rpm. Using a pipette, the bottom layer containing triflates of S-methyl or S-ethylsulfonium salts was transferred to a 2 ml plastic vial and washed three times with benzene. The resulting mixture was analyzed using Bruker SolariX XR FT/ICR mass spectrometer equipped with a 15 T superconducting magnet using ESI and MALDI ion sources.

ESI and MALDI mass spectra of model compounds derivatization products contain intense peaks of formed sulfonium salts. The ionization efficiencies of the derivatives synthesized using all tested alcohols are close, so the approach can be used for shifting the ions signals from noisy low mass region. The comparison of the results achieved using the traditionally applied alkylation by methyl iodide in presence of $AgBF_4$ and the develop approach clearly shows that the latter allows detecting higher number of sulfur compounds.

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Evaluation of new adsorbent materials for detection of oilfield volatile hydrocrabons

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Oil or gas fields are the source of a continuous diffusion of volatile hydrocarbons from underlying beds up to the earth's surface known as macro- and micro-seepages [1]. Detection of these compounds allow gathering valuable information about source (organic matter type), maturation (organic maturity), migration (migration pathway delineation) and other parameters of deposits. There are several approaches allowing detection of volatile organic compounds (VOCs) via soil and gas sampling, however most of the methods are based on the collecting and concentrating the analytes with various adsorbents. For this goal, several commercial passive gas samplers were developed and deployed [2]. Thus, variety of adsorbents-based environmental VOCs accumulation tubes were engineered, however commonly they are not specifically designed for adsorption of oilfield vapors and control of their uptake rate. In the current work, we have screened a library of carbon-based mesoporous and microporous adsorbing materials for the highest affinity towards hydrocarbons and N,S,O-bearing volatile vapors and selected two best performing sorbents. These two novel customized materials were evaluated for the affinity to vapors from fuels and natural oil samples upon micoseepage at the laboratory conditions and compared with widely used commercial adsorbent-Tenax GR.

Crude oil from Romashkinskoye field, gasoline and diesel fuels were used as models for VOCs producing. Samples of the model liquids were placed on the bottom of a glass container (0.2 m diameter, 0.5 m height) and covered with limestone fragments (fraction 5-20, layer thickness 20 cm) and sand (layer thickness 20 cm). The sorbent samples were packed in a Gore-Tex membrane based on thermo-mechanically expanded PTFE (ePTFE) to minimize its contact with water, placed into a glass beaker on the surface of the sand and held there for one week. The analysis of the retained compounds from the sorbent samples was performed using thermal desorption (Gerstel TDU 2, The initial temperature 50°C, initial time 1 min, desorption temperature 280°C, holding time 5 min, heating rate 600°C/min, transfer temperature 280°C) with the subsequent GCxGC/MS identification (Leco Pegasus BT 4D, electron ionization mode, combination of polar Rxi-17Sil (30 m ×0.25 mm ×0.25 μm) and non-polar Rxi-5Sil (2m ×0.10 mm ×0.10 μm)) columns.

The analysis of the GCxGC/MS data results demonstrated that the proposed materials allow achieving adsorbing capacity comparable and exceeding the commonly used Tenax GR. Moreover, the number of identified compounds was 10% higher in case of A4 sorbent. The achieved results clearly shows that the proposed sorbents can be successfully used for the detection of oilfield volatile hydrocarbons.

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De novo sequencing of *Rana arvalis* skin peptides with the Twister algorithm

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Skin secretion of amphibians, including Ranid frogs, is rich in biologically active peptides, thus defending the former against pathogens and predators [1]. These peptides can be used in effective drug development; however, to this end their primary structure must be established as the very first step. Since of most interest are novel compounds, this task should be accomplished through *de novo* sequencing.

Manual *de novo* sequencing of the peptides composing Ranid frog skin peptidome is tedious and time-consuming – but automated *de novo* sequencing of those is challenging for most existing algorithms because the respective peptides are non-tryptic, and due to the presence of the “Rana box” loop in certain peptide families.

In this work, we investigate the possibilities of applying the Twister *de novo* sequencing algorithm [2,3] to the analysis of endogenous frog skin peptides. The advantages of Twister over the other methods comprise the absence of *a priori* assumptions on the peptide amino acid sequence, which implies its ability to successfully retrieve long fragments of unexpected ones.

We tested the proposed approach on the data set consisting of ETD MS/MS spectra acquired on Thermo Orbitrap Elite mass spectrometer and EThcD MS/MS spectra acquired on Thermo Fusion Orbitrap mass spectrometer from the skin peptidome of Moscow and Ljubljana population of *Rana arvalis*, as described in [1]. The obtained results strongly supported the conclusions from [1]. Application of the suggested method to a new dataset collected in a similar way immediately revealed in addition the presence of Ranatuerin-T1 and its variant with a substitution V19P. Our future efforts will be concentrated on adjusting the algorithm to the case of frog skin peptidome.

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Study of photochemical oxidation of petroleum and petroleum products

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The degree of crude oil use is determined by content of non-hydrocarbon high-molecular compounds, a significant part of which are tar-asphaltene substances. Tar-asphaltene substances (TAS) represent the largest group of the most high-molecular heteroatomic compounds of crude oil. Chemical and thermal research methods are based on the destructive transformation of TAS molecules into simple fragments and their identification by various methods of analysis. However, it is known that asphaltenes, which include the above mentioned compounds, are exposed to erosion and destruction under exposure to light and air, having an impact on asphalt roads in mountainous areas. For investigation of the TAS the developed in our laboratory photochemical method was used that was different from general chemical methods by its softness of provided conditions.

The objective of the present work is to clarify the process of photochemical transformation and the structure and properties of the TAS from Georgian crude oils of various chemical types.

TAS were irradiated with a mercury quartz lamp. In the process of irradiation, the products of photochemical transformation (PPCT) were investigated every 20 hours. Methods of analysis were elemental analysis, gas-liquid chromatography and spectrometry (IR and NMR). The results of the analyses showed that during irradiation of tar-asphaltene substances in air, there can be seen photochemical destruction of molecules with emission of gaseous products, on one hand, and intensive photo-oxidative processes with formation of higher melting compounds, on the other hand.

Analysis of gaseous products showed the presence of C_1-C_4 hydrocarbons, obtained by splitting-off the alkyl substituents and cleavage of naphthenic rings. When comparing tars and asphaltenes in liquid products the OH-functional groups of phenolic and alcoholic character were found in large quantities. However, in different samples these groups were quantitatively represented differently depending both on the nature of the crude oil and on the depth of photochemical oxidation. It should be noted that 15-20% of PPCT of asphaltenes and 50-60% of tars can be dissolved in water. These mainly include hydroxyl-containing compounds. It was also determined that in the process of photochemical oxidation the saturated fragments of molecules were destroyed predominantly and the aromatic structures stayed practically unaffected.

In the process of photochemical oxidation of tar-asphaltene substances, the water soluble biologically active substances are formed, and this explains the stimulation of plant growth by high-boiling oil residues, which is observed in practice and used in agriculture.

Destructive transformation of TAS during photochemical oxidation and formation of water-soluble forms explains the destruction and erosion of mountainous asphalted roads, and formation of biologically active substances that stimulate plant growth, as well as self-purification of water basins polluted with Petroleum and Petroleum products.

High molecular heterocyclic aromatic hydrocarbons in Georgian petroleum

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Polycyclic aromatic compounds that are components of crude oils and make a lot of ecological problems are the subject of the study using various separation and mass spectrometry methods. Of particular interest are crystalline and heterocyclic aromatic compounds present in high-boiling oil fractions.

The objective of the present work was the study of the fullest possible individual composition of the aromatic compounds of crude oil by modern research methods. Polycyclic aromatic hydrocarbons isolated from vacuum gas oil fractions of Georgian Petroleum of various types (tarry, paraffinic and aromatic) had been studied by gas-liquid chromatography (GC), mass-spectrometry (MS) and cromato-mass-spectrometry (GC-MS) methods.

Experiments were performed on a GC–MS magnetic sector mass spectrometer operated at standard conditions. The GC separation was achieved on a 15 m capillary column with SE-30 using the following parameters: 100^0C at 2^0C/min to 240^0C and from 240^0C at 5^0C/min to 270^0C (14 min). Automated mass deconvolution and identification system (AMDIS) was used for data analysis. The use of AMDIS expands the limits of GC-MS application, and the use of reliable mass spectral and GC retention index libraries remains highly relevant in oil research. However, preliminary separation of components remains crucial for GC-MS application. It is obvious that the above mentioned pretreatments led to successful extraction of aromatic components from the Petroleum. In these extracts, its major components were identified: phenanthrenes, anthracenes, fluorenes, naphthalenes and biphenyls, isomeric methylindenes and dimethylnaphthalenes, acenaphthenes, anthracenes, phenanthrenes, terpenyls and their mono- and polyalkyl derivatives and hydrogenated analogues. During crystallization and recrystallization of aromatic extracts the crystals of various colors were precipitated. A large number of crystalline substances of two types: fluorescent in the visible region of the spectrum and red non-fluorescent substances were obtained the structure of which was established by X-ray diffraction analysis. It was found that the red crystals are nitrogen-containing compounds. It turned out also that fluorescent crystalline compounds were characteristic for paraffin Petroleum with low tar content; non-fluorescent nitrogen-containing crystals of red color were obtained from tarry and from aromatic Petroleum, were obtained both types of crystalline components. Structural-group composition of these components was studied by IR-, UV- and MS methods. It was established that the crystalline compounds of Petroleum are complex hybrid structure containing nuclei of naphtenes and alkylated condensed aromatic hydrocarbons. On the basis of the TIC of the crystalline samples for the first time in Georgian oils were identified the sulfur and nitrogen heteroanalogues of high-molecular polycyclic aromatic hydrocarbons: benzonaphthothiophenes in the “benzanthracene” fraction, benzocarbazole and dibenzthiophenes in the “phenanthrene” fraction. The crystals also contain phenanthrenes, anthracenes, chrysenes, pyrenes, benzpyrenes and their substituted analogues.

The use of the traditional GC-MS method made it possible to determine the composition of crystalline components of high boiling aromatic hydrocarbons in Georgian Petroleum at a molecular level and to identify the heterocyclic compounds in them for the first time.

Improving storage time and technical specifications of biodiesel

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Biodiesel is one of the most effective, affordable, alternative and renewable fuel, which can reduce great deal exploitation of fossil fuels, thus contributing to curbing greenhouse gas emissions and reduction anthropogenic global warming factors. Biodiesel could be an effective solution for energy supply diversification and energy security for the countries which almost entirely depend on imported hydrocarbons and which need to develop alternative, clean, renewable and eco-friendly fuels of their own production.

Biodiesel is based on processing renewable bio-resources; the main sources for biodiesel production are considered various plant oils. Industrial production of biodiesel is mainly based on catalyzed trans-etherification, since it is the most economically viable process requiring relatively low temperatures and pressure and producing 98% conversion. The trans-etherification process is based on the reaction of triglycerides (fat/oil) with alcohol to form esters (biodiesel) and glycerol.

The advantage of biodiesel is the fact that biodiesel is carbon-neutral, bio-degradable and less toxic fuel, therefore biodiesel is considered as one of the most environmentally friendly fuels. Biodiesel has the potential to be more widely used as alternative, eco-friendly fuel in every sector where conventional, petroleum based diesel fuel is used, especially in transport sector. The disadvantage of biodiesel, however, is the relatively short life and storage time, therefore improving the life and storage time of biodiesel, at the same time maintaining all technical parameters and high quality of the fuel, are very important for the biodiesel industry.

To solve these problems the present works offers an innovative nano-composition of biodiesel, which can significantly prolong life time of pure biodiesel fuel (i.e. B100) as well as its blends, while maintaining and even improving the main technical parameters of the fuel.

The analyzed physical-chemical characteristics of biodiesel (B100) Blend (B5, B10, B20) and those of petroleum diesel fuel, their quantitative analysis and identification of individual components were received by gas chromatography and the functional groups of these fuels were analysed using IR Fourier spectrum meter. The FTIR spectra were obtained with the aid of the Perkin Elmer Spectrum Version 10.4.2. The wave numbers arranged from 500 to 4000 cm -1.

The results of the research show that the nano-composition of biodiesel meets the demands of EN 14205, ASTM D 6751 and EN 590 standards, at the same time the life time and storage time of biodiesel has been significantly increased and in addition the physical and chemical parameters has been improved.

When comparing the physical and chemical parameters of conventional biodiesel and nanodiesel and their spectrums, it becomes obvious, that several major parameters of biodiesel have been improved, and what is important, the structural compositions remained stable; at the same the results show that there are further possibilities for improvements of several major parameters and the structural compositions of bio diesel.

The nano-composite of biodiesel will allow storage biodiesel and its blends for much longer period of time and using in almost all kind of internal combustion diesel type engines, serving as a reliable, alternative fuel for sustainable clean transport, strengthening diversification of energy supply and protecting the environment.