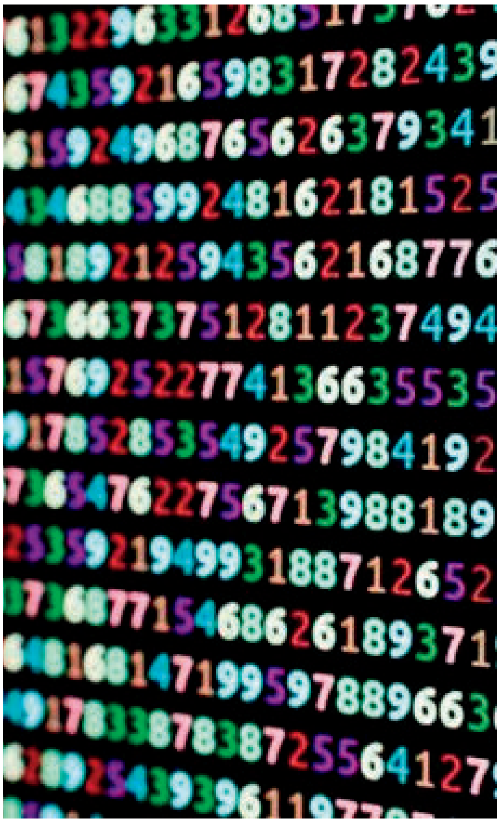

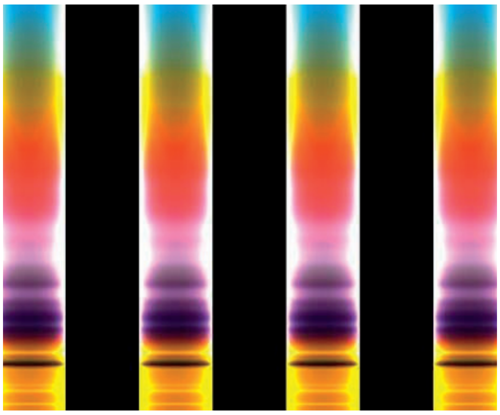

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Wednesday - June 28

8:30-9:00		Registration
9:00-10:40		Opening and Morning Session I
9:00-9:10		**Opening of the workshop**
9:10- 9:40	KNL-01	**HIGH PERFORMANCE DIRECT MS FACILITATED BY SPME PROBE** *Janusz Pawliszyn, University of Waterloo, Canada*
9:40- 10:00	L-01	**THE ROLE OF GC×GC IN MINERAL OIL ANALYSIS. APPLICATION OF A COMPLETE LC-GC×GC-FID/TOFMS PLATFORM** *Giorgia Purcaro, Gembloux Agro-Bio Tech, University of Liège, Belgium*
10:00- 10:20	L-02	**ANALYSIS OF SEMI-VOLATILES ORGANIC COMPOUNDS IN WATER SAMPLES WITH A FULLY AUTOMATED MULTI FIBER EXTRACTION APPROACH, PRELIMINARY RESULTS** *Marco Sarti, ITS Tullio Buzzi, Prato, Italy*
10:20- 10:40	L-03	**MACHINE LEARNING AND DATA CHALLENGES IN SEPARATION SCIENCE** *Agnieszka Smolinska, Maastricht University, Netherland*
10:40-11:00		Coffee break/poster session – Sponsored by Shimadzu
11:00-12:30		Morning Session II
11:00-11:30	KNL-02	**DEVELOPMENT OF ORDERED STATIONARY PHASE SUPPORTS FOR LIQUID CHROMATOGRAPHY** *Gert Desmet, Vrije Universiteit Brussel, Brussels,Belgium*
11:30-11:50	L-04	**VOLATOLOMICS OF THE OXIDATIVE STRESS AT THE MOLECULAR LEVEL USING IN VITRO MODELS** *Jef Focant, University of Liège, Belgium*
11:50-12:10	L-05	**MICROWAVE-ASSISTED SAMPLE PRETREATMENTS AND ANALYTICAL PYROLYSIS: A HOLISTIC APPROACH FOR THE STUDY OF MICROPLASTICS AND CORRELATED POLLUTANTS** *Jacopo La Nasa, University of Pisa, Pisa, Italy*
12:10-12:30	L-06	**ONLINE SPE AND LC-MS FOR PFAS ANALYSIS IN FOOD SAMPLES** *Gerd Vanhoenacker, RIC technologies, Kortrijk, Belgium*
12:30-13:45		Lunch/poster session

Wednesday - June 28

13:45-15:15		**Afternoon Session I**
13:45-14:15	**KNL-03**	**DETERMINATION OF PESTICIDES IN FOOD SAMPLES THROUGH REDUCED SAMPLE PREPARATION COUPLED TO FLOW- AND CRYOGENIC-MODULATION GC×GC COMBINED WITH TRIPLE-QUADRUPOLE MASS SPECTROMETRY** *Luigi Mondello, University of Messina, Italy*
14:15-14:35	**L-07**	**NOVEL APPROACHES IN ADDRESSING THE CHALLENGES OF MONITORING MULTIPLE CLASSES OF HALOGENATED POPS IN FOOD AND FEED** *Gauthier Eppe, University of Liège, Belgium*
14:35-14:55	**L-08**	**COUPLING VACUUM-ASSISTED HEADSPACE AND MULTI-CUMULATIVE TRAPPING SPME WITH GC×GC-MS TO ENHANCE THE CHROMATOGRAPHIC PROFILING** *Steven Mascrez, Gembloux Agro-Bio Tech, University of Liège, Belgium*
14:55-15:15	**L-09**	**POSSIBLE STRATEGIES FOR THE INCLUSION OF GLUCOSIDE CONJUGATES IN THE ROUTINE ANALYSIS OF PESTICIDES** *Ivan Aloisi, Wageningen Food Safety Research, Netherlands*
15:15-15:45		**Coffee break/poster session – Sponsored by Milestone**
15:45-17:35		**Afternoon Session II**
15:45-16:15	**KNL-04**	**HOW TO OPTIMIZE IN VIVO AND CLOSE TO IN VIVO MICROEXTRACTION METHODS FOR BIOMEDICAL RESEARCH AND CLINICAL PRACTICE** *Barbara Bojko, Nicolaus Copernicus University in Torun, Bydgoszcz, Poland*
16:15-16:35	**L-10**	**ADVANCING MICRO-POLLUTANT STRUCTURAL ELUCIDATION: INTEGRATING PREDICTIVE RETENTION TIME MODELING WITH HIGH-RESOLUTION MASS SPECTROMETRY** *Frederic Lynen, University of Gent, Belgium*
16:35-16:55	**L-11**	**COMPREHENSIVE GCXGC HIGH RESOLUTION MS AND SELECTIVE ISOLATION OF CHEMICALS IN THE INVESTIGATION OF HUMAN CHEMOSIGNALS ELICITED FROM EMOTIONAL STIMULATION** *Fabio di Francesco, University of Pisa, Italy*
16:55-17:15	**L-12**	**GOING DEEPER IN TILE-BASED PROCESSING FOR COMPLEX GC×GC-TOFMS DATASETS** *Pierre-Hugues Stefanuto, University of Liège, Belgium*
17:15-17:35	**L-13**	**USE OF HEADSPACE SPME COUPLED WITH FLOW-MODULATED COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY (ENANTIO×POLAR) WITH TIME-OF-FLIGHT MASS SPECTROMETRY TO DETERMINE CHIRAL LACTONES AND CHARACTERIZE THE VOLATILOME OF MARSALA WINES** *Micaela Galletta, University of Messina, Italy*
17:35- 19:00		**Welcome Cocktail**

Thursday- June 29

8:30-9:00		Registration
9:30-10:30		Morning Session III
9:00-9:30	KNL-05	**CHROMATOGRAPHIC-BASED ANALYTICAL DEVELOPMENTS FOR THE MOLECULAR CHARACTERIZATION OF COMPLEX MATRICES RELATED TO NEW ENERGY SOURCES** *Pierre Giusti, TotalEnergies, France*
9:30-9:50	L-14	**LINEAR AND RADIAL HPTLC COUPLED WITH HIGH RESOLUTION MASS SPECTROMETRY IMAGING** *Edwin de Pauw, University of Liège, Belgium*
9:50-10:10	L-15	**MINERAL OIL ANALYSIS IN FOOD: AN ANALYTICAL CHALLENGE** *Annelies Van Heyst, Primoris, Belgium*
10:10-10:30	L-16	**APPLICATION OF MULTI ANALYTICAL CHROMATOGRAPHY PLATFORMS AND CHEMOMETRIC PROCESSING FOR THE PHYTOCHEMICAL PROFILING OF CANNABIS SATIVA INFLORESCENCES** *Natasha D. Spadafora, University of Ferrara, Italy*
10:30-11:00		Coffee break/poster session – Sponsored by Markes
11:00-12:30		Morning Session IV
11:00-11:30	KNL-06	**CHROMATOGRAPHIC ANALYSES: AN INTEGRATED CHAIN FROM SAMPLE PREPARATION TO DATA INTERPRETATION** *Hans-Gerd Janssen, Wageningen University, Wageningen, Netherlands*
11:30-11:50	L-17	**CHALLENGES OF CHOOSING A DIFFERENT CARRIER GAS IN GC/MS: HYDROGEN OR NITROGEN?** *Jaap de Zeeuw, CreaVisions, Boxtel, Netherland*
11:50-12:10	L-18	**A NEW GREENER WAY FOR AFLATOXINS DETERMINATION IN PISTACHIO: A DEEP EUTECTIC SOLVENT–BASED APPROACH** *Andrea Schincaglia, University of Ferrara, Italy*
12:10-12:30	L-19	**MICRO THERMAL DESORPTION AS A SAMPLE INTRODUCTION TO HYPER-FAST GC** *Peter Boeker, University of Bonn, Bonn, Germany*
12:30-14:0		Lunch/poster session

Thursday- June 29

14:00-15:45		Afternoon Session III
14:00-14:30	KNL-07	**SIMULTANEOUS DETERMINATION OF FATTY ACIDS AND FATTY ACID METHYL ESTERS IN AQUEOUS SAMPLES BY HS-SPME ARROW GC-MS/MS** *Torsten C. Schmidt, University of Duisburg-Essen, Essen, Germany*
14:30-14:50	L-20	**COUPLING CAPILLARY ELECTROPHORESIS WITH ION MOBILITY MASS SPECTROMETRY: CHOOSE YOUR OWN ORTHOGONALITY FOR EXPERIMENTAL PHYSICAL CHEMISTRY OR ANALYTICAL CHEMISTRY APPLICATIONS** *Johann Far, University of Liège, Belgium*
14:50-15:10	L-21	**THE VERSATILITY OF HIGH-RESOLUTION SEPARATION TECHNIQUES FOR TARGETED AND NON-TARGETED ANALYSIS** *Flavio A. Franchina, University of Ferrara, Italy*
15:10-15:30	L-22	**COLUMN DESIGN, QUANTITATIVE ASSESSMENT OF THE 3D PORE SPACE, AND PERFORMANCE CHARACTERIZATION OF POLYMER MONOLITHIC CAPILLARY COLUMNS TARGETING HIGH-RESOLUTION PEPTIDE PROFILING** *Zhuoheng Zhou, Vrije Universiteit Brussel, Brussels, Belgium*
15:30-15:50	L-23	**COLORECTAL CANCER DIAGNOSTIC BIOMARKERS SCREENING: MULTI-MODAL METABOLOMICS & LIPIDOMICS APPROACH** *Kinjal Bhatt, OBiAChem, MolSys, University of Liège, Belgium*
15:50-16:00		Closing remarks

POSTER SESSIONS

P-01	**AROMA PROFILING OF CHOCOLATE: HOW DO PLANT-BASED AND LOW SUGAR VARIETIES COMPARE TO REGULAR MILK CHOCOLATE?** Laura McGregor, Helena Leask, James Ogden, Rachael Szafnauer
P-02	**UTILIZATION OF STIR BAR SORPTIVE EXTRACTION - GAS CHROMATOGRAPHY - MASS SPECTROSCOPY TECHNIQUE TO STUDY THE AROMA ACTIVE COMPOUND PRODUCTION DURING KOMBUCHA FERMENTATION** Sarah Suffys, Gaëtan Richard, Clément Burgeon, Pierre-Yves Werrie, Eric Haubruge, Marie-Laure Fauconnier, Dorothée Goffin
P-03	**DEVELOPMENT OF A WORKFLOW FOR THE CHARACTERIZATION OF PYROLYSIS OILS FROM PLASTIC WASTE USING MULTIDIMENSIONAL GAS CHROMATOGRAPHY AND MASS SPECTROMETRY** Monica Romagnoli, Alberto Cavazzini, Flavio A. Franchina
P-04	**EXPLOITING SORBENT-BASED SAMPLING AND SINGLE-STAGE THERMAL DESORPTION COUPLED TO COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY TO PROFILE THE SCENT OF FLORAL PARTS FROM CANNABACEAE SPECIES** Marco De Poli, Damiana Spadafora, Simona Felletti, Flavio A. Franchina
P-05	**AROMA COMPOUNDS IN BALSAMIC VINEGARS: OPTIMIZATION OF HEADSPACE SOLID-PHASE MICROEXTRACTION (HS-SPME) FOR MULTIDIMENSIONAL GAS CHROMATOGRAPHY COUPLED WITH MASS SPECTROMETRY (GC×GC-MS) ANALYSIS** Sofia Malcangi, Alberto Cavazzini, Flavio A. Franchina
P-06	**EVALUATION OF VOLATILE COMPOUNDS IN COCOA BEANS (THEOBROMA CACAO L.1753) FROM NEW FERMENTATION MEDIA IN IVORY COAST** Kouakou Ahossi Konan, Ibourahema Coulibaly, Marie-Laure Fauconnier
P-07	**ENHANCED ANALYTE EXTRACTION WITH AUTOMATED MULTI-PHASE HIGH-CAPACITY SORPTIVE EXTRACTION (HISORB) FOR GC-MS** Rachael Szafnauer, Lucy Hearn, Jan Peter Mayser, Tomas Kovalczuk
P-08	**A NOVEL EI SOURCE OPTIMIZED FOR USE WITH HYDROGEN CARRIER GAS IN GC/MS AND GC/MS/MS** Wannes Vandebroeck, Remko van Loon
P-09	**ANTIPLASMODIAL-GUIDED INVESTIGATION OF LANTANA CAMARA (VERBENACEAE)** Pierre Leonel Taguimjeu Tafokeu K., Yannick Stéphane Fotsing Fongang, Silvère Augustin Ngouela, Marie-Laure Fauconnier
P-10	**UNDERSTANDING CONSUMER PREFERENCE OF HARD SELTZER DRINKS USING ADVANCED ANALYTICAL TOOLS WITH SENSORY DATA CORRELATION** Rachael Szafnauer, Lucy Hearn, Laura McGregor, Natasha Spadafora
P-11	**APPLICATION OF 2D-LC WITH MS DETECTION WITH SUPERFICIALLY POROUS COLUMNS TO THE ANALYSIS OF COLD MEDICINE** Wannes Vandebroeck, Danny van Oevelen
P-12	**COMPARISON OF DIFFERENT SAMPLE PREPARATION PROTOCOLS FOR HIGH-SENSITIVITY DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN VEGETABLE OILS** Merve Kazanci, Laura Barp, Chiara Conchione, Sabrina Moret

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P-14	**FUNGAL VOLATILE ORGANIC COMPOUNDS: NEW TARGETS FOR THE DETECTION OF FUNGAL CONTAMINATION AND MYCOTOXIN PRODUCTION** Laurie Josselin, Caroline De Clerck, Marthe De Boevre, Hélène Soyeurt, Antonio Moretti, Marie-Laure Fauconnier
P-15	**STUDY OF THE FORMATION OF PERFLUOROALKYL CARBOXYLIC ACID (PFCA) DIMERS IN GAS PHASE BY COUPLING ION MOBILITY WITH MASS SPECTROMETRY (IM-MS)** Aurore Schneiders, Johann Far, Edwin De Pauw, Lidia Belova, Adrian Covaci, Gauthier Eppe
P-16	**STABILITY STUDY OF MULTIPLE PESTICIDES IN PASSIVE SILICON WRISTBAND SAMPLERS OVER TIME AT ROOM TEMPERATURE AND AT - 20°C IN A POTATO CULTIVATION CONTEXT** Chaymae El Amraoui Aarab, Laure Joly, Jessica Marchi
P-17	**FRACTIONATION OF ROSEMARY SOLID RESIDUE FROM STEAM DISTILLATION: THE RELATIONSHIP BETWEEN PHENOLIC PROFILE AND BIOLOGICAL ACTIVITIES** Imane Ziani, Genva Manon, Hamza Bouakline, Oumayma Sayah, Marie Laure Fauconnier, Ali EL Bachiri
P-18	**SLIDING WINDOWS IN ION MOBILITY (SWIM): A NEW APPROACH TO INCREASE THE SEPARATION POWER IN TRAPPED ION MOBILITY-MASS SPECTROMETRY HYPHENATED WITH CHROMATOGRAPHY** Hugo Muller, Georges Scholl, Johann Far, Edwin De Pauw, Gauthier Epp
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P-26	**DIVERSE APPROACHES TO CAPTURING BACTERIAL VOLATILES IN APHID HONEYDEW: METHODOLOGICAL COMPARISONS** Jiahui Liu, Lallie Glacet, Frederic Francis
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P-28	**NOVEL APPROACHES FOR CRITICAL QUALITY ATTRIBUTE DETERMINATION FOR THERAPEUTIC ANTIBODIES, ANTIBODY-DRUG CONJUGATES, AND OLIGONUCLEOTIDES** A. Egberts, C. Muraco, B. Peters
P-29	**CHARACTERIZATION AND DIFFERENTIATION OF CHINESE ‘BAIJIU’ LIQUOR APPLYING SPME COUPLED TO COMPREHENSIVE TWO-DIMENSIONAL CHROMATOGRAPHY AND TIME-OF-FLIGHT MASS SPECTROMETRY (GC×GC-TOFMS)** Lena Dubois, Sebastiano Panto, Nick Jones, Dmitrii Rakov, Henryk Jeleń, Xi H
P-30	**UNLOCKING THE AROMA COMPOUNDS OF PISTACHIOS USING THE POWER OF MULTI-DIMENSIONAL GAS CHROMATOGRAPHY** Andrea Schincaglia, Giorgia Purcaro, Marco Beccaria
P-31	**EXPLORATION OF THE SAPONIFICATION CONDITIONS FOR MINERAL OIL ANALYSIS THROUGH THE UTILIZATION OF MICROWAVE-ASSISTED SAPONIFICATION/EXTRACTION** Grégory Bauwens, Giorgia Purcaro
P-32	**QUALITATIVE SCREENING OF CATALYTIC PYROLYSIS WOOD OIL BY MEANS OF GC×GC-TOFMS, SOFT IONIZATION, AND DIFFERENT COLUMNS SETUP** Marco Piparo, Pierre Giusti, Sabrina Marceau, Jean Francois Focant, Giorgia Purcaro, Eliane Lazzari
P-33	**CONTRIBUTION OF ATMOSPHERIC PRESSURE CHEMICAL IONIZATION MASS SPECTROMETRY FOR THE CHARACTERIZATION OF BIO-OILS FROM LIGNOCELLULOSIC BIOMASS: COMPARISON WITH ELECTROSPRAY IONIZATION AND ATMOSPHERIC PRESSURE PHOTOIONIZATION** Charlotte Mase, Marco Piparo, Pierre Giusti, Carlos Alfonso
P-34	**ENHANCED SAMPLE PREPARATION OF ENVIRONMENTAL MATRICES WITH MICROWAVE ASSISTED EXTRACTION** Diego Carnaroglio
P-35	**FAST AND RELIABLE FATTY ACID METHYL ESTER (FAME) DETERMINATION IN FOODSTUFF BY MICROWAVE SAMPLE PREPARATION** Diego Carnaroglio
P-36	**COMPARISON OF DIFFERENT EXTRACTION METHODS FOR THE DETERMINATION OF FATTY ACID METHYL ESTERS IN MUSSELS SAMPLES** Donatella Ferrara, Giulia Giacoppo, Marco Beccaria, Giorgia Purcaro
P-37	**POTENTIALITIES OF HIGH-CAPACITY-HEADSPACE-EXTRACTION FOLLOWED BY GC×GC-QMS TO BETTER APPRECIATE COFFEE BREW NOTE** Damien Eggermont, Steven Mascrez, Giorgia Purcaro
P-38	**ANALYSIS OF SEMI-VOLATILES ORGANIC COMPOUNDS IN WATER SAMPLES WITH A FULLY AUTOMATED MULTI FIBER EXTRACTION APPROACH, PRELIMINARY RESULTS.** Marco Sarti, Simona Bettarini, Andrea Carretta, Stefano Dugheri

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Keynote lecture

KNL-01

High-Performance Direct MS Facilitated by SPME Probe

Janusz Pawliszyn

University of Waterloo, Waterloo, Canada

Abstract

Recent worldwide efforts toward the implementation of sustainable technologies will have an impact on the future practice of analytical chemistry. The two most important directions in green analytical chemistry are to facilitate high throughput lab determination and move the analytical process on-site and in-vivo. To address this need, we have developed screening approaches via direct coupling of SPME to MS. Matrix-compatible coatings provide clean extraction suitable for directly introducing extracted compounds to mass spectrometers resulting in the elimination/minimization of any matrix effects associated with ion suppression. In the presentation, we will discuss diverse SPME-based devices recently developed in our laboratory for the extraction/enrichment of analytes of interest from tissue and small volumes of complex sample matrices, which can be directly coupled with mass spectrometry instruments for rapid analysis. The approaches tested include Coated Blade Spray (CBS), SPME-transmission mode-direct-analysis-in-real-time (SPME-TM-DART-MS), SPME- microfluidic open interface (SPME-MOI). Total analysis time for manual operation is typically 5 minutes but does not exceed 15 minutes and sample volumes range between 1-100 µL to the whole live organs. Sampling/sample preparation is performed either by spotting the sample onto the SPME-device, or by immersing the SPME probe in a vessel containing the sample or placed directly into tissue. Despite short extraction times, limits of detection in the sub-ng/mL range were obtained, while good accuracy, and linearity was attained for all the studied probes (e.g., therapeutic drugs, drugs of abuse, immunosuppressants, veterinary drugs, and pesticides) in the diverse matrices scrutinized (e.g., urine, plasma, blood, saliva, brain, muscle, fruits, meat, and other tissues). The fully automated version of the sample preparation workflow allows for a total extraction time of less than 1 min per sample when 96 extractions are simultaneously conducted, while the direct-to-MS workflow allows for screening in both negative and positive ionization modes.

KNL-02

Development of Ordered Stationary Phase Supports for Liquid Chromatography

Gert Desmet, Bert Vankeerberghen

VUB, Brussels, Belgium

Abstract

Liquid chromatography has significantly evolved over the last century and is today a mainstream working horse for chemical analysis in the (bio)pharmaceutical, chemical, food and other industries. However, the chromatographic separation performance still suffers from randomness of the particle packing in. This issue can be resolved by changing to another column format, such as multi-capillary columns. In practice however, the polydispersity effect, which emanates from the inevitable small differences in capillary diameter, completely ruins the potential gain in separation performance.

In this contribution, we prove that the polydispersity effect can be countered by introducing a diffusional crosstalk between the different channels of a multi-capillary column. This has been performed by a fluorescence microscopy-based dispersion study of silicon-micromachined microfluidic chips, mimicking a total of 8 different multi-capillary chromatography systems. The experimental results have moreover been used to validate analytical expressions regarding dispersion in multi-capillary flow systems.

Another way to perfectly ordered columns consists of using micromachined and electrochemically anodized micro-pillar array columns. A first generation of these µPAC's was introduced a couple of years ago and found adoption in proteomics research. Recently, a second µPAC generation has been introduced where the characteristic dimensions (pillar diameter and interpillar distance) have been halved. We provide an on-chip comparison of this new generation compared to the first generation. The observed reduction of H with a factor of 2 around the uopt-velocity and with a factor of 4 in the C-term dominated regime of the van Deemter-curve is in full agreement with the theoretically expected gain. Compared to Gen 1, Gen 2 offers a 4-fold reduction of the required analysis time around the optimal velocity and about a 16-fold reduction in the C-term-dominated range.

KNL-03

Determination of pesticides in food samples through reduced sample preparation coupled to flow- and cryogenic-modulation GC×GC combined with triple-quadrupole mass spectrometry

M. Zoccali[1], Alessia Arena[2], Antonio Ferracane[2], Peter Q. Tranchida[2], Luigi Mondello[2,3]

[1]Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Università degli Studi di Messina, Messina, Italy. [2]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche e Ambientali, Università degli Studi di Messina, Messina, Italy. [3]Chromaleont s.r.l., c/o Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche e Ambientali, Università degli Studi di Messina, Messina, Italy

Abstract

Nowadays, the trends in the field of "Green Chemistry" are simplicity and rapidity of the analytical methods and the reduction of organic solvent consumption. For this reason, the aim of the present study was the development of a low solvent amount consuming sample preparation for the analysis of target xenobiotics in vegetable products and different kind of vegetable oils by using both flow- and cryogenic-modulation comprehensive two-dimensional gas chromatography (CM GC × GC) combined with triple quadrupole mass spectrometry (QqQMS).

Vegetable samples were analyzed using a "reduced-scale" QuEChERS extraction method and flow-modulated GC×GC-QqQMS. While the oil samples were only treated with limited volumes of acetonitrile (500 µL), analyte introduction onto the first dimension column was performed through a programmed-temperature vaporizer (PTV). The exploitation of cryogenic modulation and QqQMS (in the multiple-reaction-monitoring mode) eliminated the need of a target-analyte concentration step. Furthermore, the use of two analytical columns with a high thermal stability and with a thin film thickness, enabled the elution of high boiling-point matrix interferences.

The GC×GC-QqQMS methods developed were demonstrated to be suitable for the trace level determination of food samples contaminants, in relation to maximum residue limits set by the European Union.

KNL-04

How to optimize in vivo and close to in vivo microextraction methods for biomedical research and clinical practice

Barbara Bojko

Nicolaus Copernicus University in Torun, Bydgoszcz, Poland

Abstract

Advances in analytical chemistry enable to make new discoveries in the area of biomedical research. One of such advances is miniaturization, which is not only greener and more environmentally friendly, but it also offers lower sample consumption and no- or minimum invasiveness of sampling. The example of sampling and sample preparation tool in bioanalysis, which fulfils these characteristics is solid phase microextraction, SPME. The technology itself is relatively well known in "conventional" analysis of collected biofluid samples, but in recent years several novel strategies of utilizing SPME in biomedical research as well as clinical practice have been explored. The most unique approach is to use SPME as "chemical biopsy" for extraction of small molecules directly from intact tissues or organs in vivo or in situ. Minimum invasiveness permits to conduct temporal and spatially resolved analysis, however optimization of extraction time and coating length in order to achieve satisfactory results demands deep understanding of the technique fundamentals. Moreover, using microextraction devices for in vivo studies under the sterile conditions of surgery room carries additional restrictions. During the talk, the abovementioned requirements and the solutions how to meet them will be discussed based on the up-to-date studies. In addition, advancements in SPME-based methods for rapid intra-surgical determination of target compounds will be presented. At the end, application of the described solutions in animal studies will be demonstrated.

KNL-05

Chromatographic-based analytical development for the molecular characterization of complex matrices related to new energy sources

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Abstract

Due to both human population growth and expanding industrial activities in the world, energy demand is constantly increasing. Renewable energy development to replace fossil-based ones is a current major challenge. Animal fats as well as vegetable oils, but also biomass pyrolysis oils, represent interesting new sources to produce biofuels. These new feedstocks contain a wide range of contaminants that can affect their physical properties. For example, higher acid content can cause severe corrosion in the engines, impact the catalytic upgrading processes. An exhaustive characterization by GC(xGC) coupled with MS of these compounds was made. In addition to these targeted impurities, molecule family type speciation was performed as it is key for modeling biofuel properties.

Despite the powerful GC×GC-MS based approach, there is still a lack in the detection heteroatoms compounds. In fact, they are split into a myriad of compounds due to the random character of the chemical processes typically involved in their production and therefore require ultra-sensitive approaches for their characterization. For this reason, a new GC detector able to provide compound-independent quantification of C, H, N, S in complex samples has been developed. It this therefore possible to achieve a species-independent generic and simultaneous quantification of C, H, N, and S. Importantly, GC-combustion-MS can be used as well for the detection of oxygen if enriched 18O-oxygen is used for the combustion.

Nevertheless, understanding the complete molecular composition of new feedstocks necessitates the use of complementarity analytical techniques. In this regard, FT ICR-MS emerges as a powerful tool for comprehensive molecular attribution of a sample. Using soft ionization processes coupled to FTICR-MS, an in-depth molecular characterization of various samples can be made.

KNL-06

Chromatographic analyses: An integrated chain from sample preparation to data interpretation

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Abstract

Chromatographic analyses consist of a number of sequential steps. Sampling marks the start of the analysis and is followed by sample preparation, sample introduction, separation, detection and chromatogram- and data interpretation. Each step is important and needs to be optimized carefully. However, if this is done in an isolated manner without considering the characteristics of the other steps, this is likely to result in a non-optimum or needlessly complex overall method. Clearly the various steps are mutually dependent. As an example, split injection on a non-polar GC column requires much less sample clean-up than in case of on-column injection on a vulnerable chiral GC column. Or focusing on the separation step: using a highly selective accurate mass spectrometer as the detector significantly reduces the requirements to be imposed on the chromatographic separation step, or on the removal of interferents in the sample preparation.

In the presentation we will take a fundamental look to sample preparation. In particular we will look to how the characteristics of the other steps in the GC analysis determine the requirements to be imposed on the sample preparation method. Key reasons why sample preparation is needed are identified. These include the need to liberate the compounds of interest from the matrix, the removal of compounds that would damage the chromatographic column or detector, preconcentration, removal of interferents etc. It is then discussed how recent developments in sample introduction, detection and separation impact on the sample preparation. This is all illustrated with examples from food quality research, petrochemistry and environmental analysis.

KNL-07

Simultaneous Determination of Fatty Acids and Fatty Acid Methyl Esters in Aqueous Samples by HS-SPME Arrow GC-MS/MS

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Abstract

Fatty acids (FAs) and fatty acid methyl esters (FAMEs) are important substance classes for example in the food industry, medicine, microbiology, water analysis, and biodiesel production. FAs mostly occur in higher concentrations than FAMEs and are in general more intensively studied. However, FAs and FAMEs are related and often appear together, as they can easily be transferred into each other. Therefore, the simultaneous determination of both compound classes would be beneficial, but so far, no established method exists for that purpose. One reason for this may be that generally methyl esterification is utilized as a derivatization technique for FAs in GC analysis, which makes it impossible to distinguish the FAs and FAMEs.

Our new method for that purpose was fully automated using a RTC PAL autosampler with various modules and combines in-situ derivatization with solid-phase microextraction arrow. Method parameters were in general optimized by design of experiment. For the simultaneous analysis of FAs and FAMEs, a GC-MS/MS method operating in MRM mode was developed.

The FAs were transformed to d_3-FAMEs in an in-situ derivatization reaction in water and could be selectively distinguished from FAMEs by the chromatographic isotope effect resulting in a retention time shift of $\Delta Rt = 0.03$ min and the mass shift of +3 m/z. The optimal derivatization conditions were found to be 20 min, 50 °C, 4 v/v% CD3OD, and pH 2.1. Method validation showed good linearities and method detection limits of FAs and FAMEs in different matrices. FAs and FAMEs were detected and quantified in different real water samples such as surface water, wastewater treatment plant effluent, and bioreactor liquids, underlining that a simultaneous measurement of both compound classes is indeed useful for various applications.

Lecture

L-01

The role of GC×GC in mineral oil analysis. Application of a complete LC-GC×GC-FID/ToFMS platform

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Abstract

Hyphenated techniques, such as LC-GC and comprehensive GC×GC, were introduced in the 1980s and 1990s, respectively. Initially, LC–GC systems were extensively studied in the 1980s and 1990s by Grob and his group, but, since perceived as too difficult, it was commercially discontinued. On the other hand, GC×GC has experienced significant growth since its introduction by Phillips in 1991, and it has now become a mature and reliable technique suitable for routine applications.

LC-GC gained renewed interest when the issue of mineral oil contamination (MOSH and MOAH) gained public attention around 2008-2009. This hyphenated system proved to be the most suitable solution for the routine analysis of mineral oil in food. However, due to the complexity of these contaminants and the interferences co-extracted from food, as well as limitations associated with mass spectrometry, even more powerful chromatographic techniques are required.

In this context, the combination of two-dimensional techniques, namely LC-GC and GC×GC, offers significant advantages. The LC-GC×GC system, coupled with both time-of-flight mass spectrometers (ToFMs) and flame ionization detectors (FID), allows for enhanced characterization of complex samples. It enables efficient sample clean-up and/or group-type separation of analytes in the LC dimension, as well as improved separation in the GC×GC dimension.

This fully integrated platform has been validated for routine use and offers several benefits. It enhances the comprehensive characterization of complex samples and simplifies sample pre-treatment. Furthermore, it provides a more robust and validated approach for routine analysis in the challenging field of mineral oil analysis in food.

L-02

Analysis of Semi-Volatiles Organic Compounds in water samples with a fully automated multi fiber extraction approach, preliminary results

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Abstract

Water analysis for semi-volatile organic compounds (SVOCs) is a challenging and labour-intensive task, due to the low limits of quantitation required. In order to reduce the amount of space and time required, to further minimize human errors and environmental impact of analysis process, a fully automated and modular at instrument sample preparation and extraction method by solid phase microextraction (SPME) before GC-MS/MS analysis is proposed for polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), phenols, polybrominated diphenyl ethers (PBDE), aromatic amines and pesticides. Working with both traditional and arrow SPME fibers automatically switched when needed thanks to Multi Fiber Exchange (MFX) all the extraction parameters have been optimized in order to minimize analysis time and maximize sensitivity for all proposed analytes. To increase versatility 2 different approaches have been evaluated: headspace-SPME sampling (HS-SPME) ad/or direct immersion-SPME (DI-SPME), both are proposed for some analytes.

Preliminary studies have shown excellent results and possibility for further improvement in the nearest future.

L-03

Machine Learning and Data challenges in separation science

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Abstract

Machine learning (ML) techniques have revolutionized the field of separation science by addressing data challenges associated with the analysis of volatile organic compounds (VOCs) in exhaled breath and feces. The alignment, peak integration, supervised techniques validation and normalization are just few aspects of data challenges in the separation science.

Alignment is a crucial step in aligning chromatographic peaks to accurately identify and quantify VOCs. ML algorithms, such as dynamic time warping and iterative peak alignment, have been employed to align chromatographic data, improving the accuracy of peak identification and integration. Peak integration plays a pivotal role in quantifying VOC concentrations. ML techniques, including neural networks and Gaussian mixture models, have been utilized for peak integration, reducing errors caused by noise, baseline fluctuations, and overlapping peaks. Yet, they all have their limitations that should be always kept in mind.

Supervised ML techniques such as classification methods are essential for identifying and distinguishing VOC patterns associated with specific health conditions. ML algorithms, such as support vector machines and random forests, have been employed to classify VOC profiles and identify potential biomarkers for diseases like lung cancer or gastrointestinal disorders, aiding in early diagnosis and personalized treatment. ML techniques, such as cross-validation and bootstrapping, have been utilized to assess the performance of ML models and estimate prediction errors, and optimize model parameters, enhancing the robustness of VOC analysis. Yet, the proper validation is often a bottleneck and overlooked problem.

In conclusion, the integration of ML techniques in separation science has significantly advanced VOC analysis in exhaled breath and fecal samples. ML algorithms have proven effective in alignment, peak integration, classification methods, validation, and normalization, enabling accurate identification, quantification, and classification of VOCs.

L-04

Volatolomics of the oxidative stress at the molecular level using in vitro models

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Abstract

Oxidative stress is a pathological condition that arises when there is an imbalance between reactive oxygen species (ROS) production and cellular detoxification ability. This condition has been linked to various diseases such as asthma and cancer, making it an important area of research for better diagnosis and treatment of inflammatory diseases. In vitro cell cultures have become an essential tool to comprehend the intricate mechanisms of oxidative stress involved in inflammatory reactions. The use of in vitro cell cultures provides an ethical and controlled environment where the effects of oxidative stress can be studied independently of other confounding factors. Volatolomics, the analysis of volatile organic compounds (VOCs) emitted by biological systems, represents a promising approach for the non-invasive, fast, and cost-effective diagnosis of diseases. The objective of this study is to gain a better understanding of oxidative stress at the molecular level by inducing chemical and biological stress on epithelial cells in vitro to mimic in vivo stress and characterize VOCs released during the process. Specifically, A549 cells were subjected to chemical and asthma-like biological stress. The VOCs released were characterized using solid phase micro-extraction (SPME) coupled with comprehensive two-dimensional gas chromatography and time-of-flight mass spectrometry (GC×GC-TOFMS). Following optimization of the conditions, we observed an increase in cell proliferation and VOC production in response to exposure to hydrogen peroxide (H2O2) and inflammatory sputum. Some of the identified biomarkers have previously been reported as potential indicators for lung diseases, including two that were highlighted as potential asthma biomarkers in a previous study. Furthermore, to determine if there is a unique signature that is cell-dependent, these conditions were applied to three epithelial colorectal cell lines, HT-29, Caco-2, and HCT116. This ongoing study aims to provide a better understanding of the molecular mechanisms involved in oxidative stress.

L-05

Microwave-assisted sample pretreatments and analytical pyrolysis: a holistic approach for the study of microplastics and correlated pollutants

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Abstract

Sampling, separation, detection and characterization of micro- and nano-plastic pollutants is a challenging and critical goal, fundamental to assess their amount, fate, and the related hazards for ecosystems. While an increasingly large number of studies are focused on determining the distribution and concentration of plastic microparticles in different environmental compartments, there is still a major lack of understanding of the most relevant mechanisms of interaction and exchange of this class of pollutants with the environment and with organisms. In the last years we observed an increase of the studies focused on the evaluation of the chemical species associated with the presence of microplastics in the environment, such as plasticizers, low molecular weight degradation products, adsorbed persistent organic pollutants, aliphatic aromatic hydrocarbons, and volatile organic compounds. In this work we combined microwave-assisted extraction and digestion, together with analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS), to study and quantify microplastics together with different classes of associated pollutants, in different environmental and biological samples. This approach can be potentially used to characterize and quantify together with microplastics, the presence of soluble oxidation products from polymers, polymer additives (phthalate plasticizers), polycyclic aromatic hydrocarbons, and polychlorinated biphenyls. The combination of the microwave-assisted treatment and the combined analytical approaches based on pyrolysis achieved significant information for a better understanding of the chemical nature of degradation products potentially released by the different polymers present as microplastics in the environment, and of the possible presence of other chemical species that are generally neglected in the study of microplastics.

L-06

Online SPE and LC-MS for PFAS analysis in food samples

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are a class of highly fluorinated chemicals which comprises a wide variety of substances, differing in chain length and branching, fluorination, functional groups, etc. Due to their unique tension-active properties - PFAS are water, oil, and dirt repellent - as well as their heat resistance, they were and still are used in various consumer and household goods and industrial products and processes.

The compounds are highly soluble and persistent, and they are ubiquitous in the environment. PFAS can be found in water, soil and sediment, waste, and even in air. They are also bio-accumulative and significant levels are detected in humans, plants, and animals and in food and feed. Due to the persistence and stability, they are considered as forever chemicals. PFAS are proven to be toxic and hence, the above-described omnipresence is problematic. As a consequence, there is a need for analytical solutions to enable sensitive analysis of numerous PFAS in a large variety of matrices.

Official guidelines and validated methods are in place for the analysis of PFAS in water and soil samples, and the number of tests carried out is ever-increasing. Their analysis in biological matrices and in food and feed samples is gaining interest and especially sample preparation is a critical part in the methodologies under development. In the work presented here, PFAS are extracted from different food types of animal origin using a QuEChERS-like approach followed by online SPE cleanup and LC-MS/MS. The online SPE approach enables to effectively reduce matrix effects and to reach the required quantification limits.

L-07

Novel approaches in addressing the challenges of monitoring multiple classes of halogenated POPs in food and feed

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Abstract

The research developed aims at combining an analytical method coupling Gas Chromatography (GC) with trapped ion mobility (TIMS)-Time of Flight Mass Spectrometry (ToFMS), i.e., GC-APCI-TIMS-ToFMS instrumentation applied to face the challenge of increasing number of persistent organic pollutants (POPs) to monitor in food and feed. A mixture of 175 POPs, including dioxins (Cl, Br or mixed), furanes (Cl, Br or mixed), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) was tested. In TIMS mode, Collision Cross Sections (CCS) versus m/z trendlines were examined in detail. The power fit functions highlighted that each class of contaminant was characterized by its own trendline. In addition, the primary factor contributing the difference in CCS among a family of halogenated compounds was discernibly identified as the halogenation degree, while the fine ion mobility separation of isomeric congeners could also be related to key structural parameters such as the number of chlorine/bromine atoms in ortho position for PBDEs, PCBs or next to the oxygen atom for PXDFs. In addition, the ion mobility resolution provided by TIMS proved valuable in deconvoluting the signal from isobars compounds that were not separated by either the GC conditions used here or the high resolution ToF MS. Further exploration showed that a correlation exists between GC retention time and ion mobility drift time (or collision cross section, CCS values). We introduced a novel concept called "Sliding Windows in Ion Mobility", SWIM. SWIM mode uses narrow and mobile ion mobility windows that are continuously scanned and adapted to the ion mobility range and GC elution time of the targeted analytes throughout the entire GC run. This new acquisition mode shows great potential to further enhance the ion mobility resolution and performance of the TIMS for the analysis of persistent organic pollutants and related emerging classes of compounds.

L-08

Coupling vacuum-assisted headspace and multi-cumulative trapping SPME with GC×GC-MS to enhance the chromatographic profiling

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Abstract

HS-SPME is a convenient and selective method for analyzing semi-volatile and volatile compounds without using solvents. However, when analyzing volatile compounds, it typically requires long equilibration times, which can be impractical for routine applications. Thus, a trade-off between sensitivity and extraction time becomes necessary.

Recently, two approaches have been proposed to enhance extraction kinetics and overall yield: vacuum-assisted HS-SPME (Vac-SPME) and multi-cumulative trapping SPME (MC-SPME). Vac-HS-SPME offers comparable or increased extraction yield while using shorter times and lower temperatures compared to traditional HS-SPME conditions [1]. Similarly, MC-SPME has the potential to improve sensitivity by using cumulative shorter extraction times instead of a single prolonged extraction [2]. Both methods have significantly enhanced the extraction of semi-volatile compounds, allowing for a more comprehensive characterization of the aroma profile.

In this study, we present a combined approach called Vac-MC-SPME, which combines Vac-SPME and MC-SPME. This approach is complemented by the improved separation capabilities of multidimensional comprehensive gas chromatography (GC×GC) equipped with a reversed fill/flush flow modulator, and advanced tile-based data handling. By comparing the results obtained using each individual sampling technique separately and focusing on targeted key compounds for defining olive oil aroma, we demonstrate the synergistic effects of Vac-MC-SPME. Furthermore, the entire chromatographic fingerprint obtained through GC×GC is utilized to differentiate between different olive oil qualities, evaluating the performance of Vac-SPME, MC-SPME, and Vac-MC-SPME approaches.

L-09

Possible strategies for the inclusion of glucoside conjugates in the routine analysis of pesticides

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Abstract

Glucosides are plant conjugates and the main secondary plant metabolites. Currently, the residues definition and the maximum residue levels of many acidic pesticides include conjugates besides the parent compound. Different strategies can be employed to include these metabolites in the routine scope. The analysis of glucosides as such is only achievable for a restricted number of compounds for which the analytical reference standards are available. In most cases, only indirect determination is by hydrolysis and determination of total parent pesticide. Hydrolysis can be done chemically by the use of strong acidic and/or alkaline conditions, or enzymatic deconjugation. Both approaches will be discussed along with their pros and cons, with emphasis on a novel methodology based on the use of a specific enzyme.

L-10

Advancing Micro-Pollutant Structural Elucidation: Integrating Predictive Retention Time Modeling with High-Resolution Mass Spectrometry

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Abstract

Implementing effective environmental management strategies necessitates a thorough understanding of the chemical composition of environmental pollutants, particularly in complex mixtures. Utilizing high-resolution mass spectrometry in combination with predictive retention index models can provide valuable insights into the structural formulas of environmental contaminants. However, accurate identification of isomeric structures can be challenging, because they usually also exhibit similar fragmentation patterns. Liquid chromatographic retention, determined by the size, shape, and polarity of the analyte and its interactions with the stationary phase, contains valuable 3D structural information that is vastly underutilized. Therefore, an LC-HRMS predictive retention index model to assist in the structural elucidation of unknowns. The approach is currently restricted to carbon, hydrogen, and oxygen-based molecules <500 g mol-1. The methodology is therein filtering out the less probable structural formulas for the elemental compositions proposed by HRMS. The possible structures are selected from public databases. The LC method is built around a broadly used reversed phase column, on which a full gradient is applied allowing spanning a broad accessible polarity range. Based on the retention (index) data for 101 solutes a Quantitative Structure-Retention Relationship is constructed. The method is able to filter out large number of erroneous structures when applied to sets of unrelated test compounds. By providing a standard operating procedure, this approach can be easily replicated and applied to various analytical challenges, further supporting its potential for broader implementation.

L-11

Comprehensive GC×GC high resolution MS and selective isolation of chemicals in the investigation of human chemosignals elicited from emotional stimulation

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Abstract

An update from the Potion project, which is investigating compositional changes of sweat volatiles in 40 volunteers undergoing fear stimulation to demonstrate the existence of human chemosignals affecting the emotional state of a receiver [1]. Upon collection from apocrine sweat glands in the armpit by pre-treated pads, chemicals were collected and then extracted, enriched, and trapped into Tenax GR tubes with dynamic headspace (DHS at 60°C). Analyses were carried out by comprehensive two-dimensional gas chromatography (GCxGC) and time-of-flight mass spectrometry (TOF), whereas emotions were induced by immersing individuals wearing mobile sensors (EDA, ECG, respiratory rate) in virtual reality scenarios. Emotional rankings showed the successful induction of fear. Out of 364 detected compounds (311 identified, 38 assigned to class, 15 true unknowns), a subset of 287 sweat volatiles showed significantly different concentration values compared to field blanks (fold change $FC < 3.0$, $p.FDR < 0.05$) [2] and 24 were significantly increased during fear vs. relaxed condition (FC: 2.21 ± 0.78, $p.FDR.BH < 0.05$, with paired t-tests). Lab-made modifications of the GCxGC setup allowed to selectively isolate a number of these chemicals for tests on human volunteers [3]. Real time measurements by proton transfer reaction time of flight confirmed that the concentration of these chemicals change when volunteers experience fear in the virtual scenario.

References:

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L-12

Going deeper in tile-based processing for complex GC×GC-TOFMS datasets

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Abstract

In the quest of making multidimensional chromatography (MDC) a robust method for untargeted screening of small molecules, one of the key remaining challenges to tackle is reproducibility. To reach this objective, important analytical aspects, such as column dimension and separation conditions need to be investigated. The biggest challenge for MDC is nevertheless data processing, meaning transforming row data into pertinent information. To enable data analytical method and processing workflow evaluation, a reference data set is required. In this study, we used a whole stool research grade test materials (RGTMs) prepared by NIST for interlaboratory studies to develop a control data set covering sampling, analysis, and processing workflows. The RGTMs contain two diets, vegan and omnivore, and two sample formats, liquid vs lyophilized. In this presentation, we will focus on the utilization of data produced from RGTMs to evaluate data processing approaches.

The robustness of several statistical workflows involving commercial, in house, and open-source solutions were investigated. First, we investigated user impact on a well-established ANOVA-based workflow. The key was to evaluate the weight of human decision on the final classification metrics and the impact on the identification of significant features. Our well-established workflow shown to be unimpacted by human decision during data cleaning, pre-processing and model building as no significant output changes appeared in the study.

Next, we developed and evaluated a new processing approach combining tile-based image comparison and machine learning-based feature selection. The combination of tile-based alignment and random forest classification increased the robustness, compared to the ANOVA-based approach. Indeed, the false positive rate decreased during feature selection, and we were able to conduct unbalanced data set processing.

L-13

Use of headspace SPME coupled with flow-modulated comprehensive two-dimensional gas chromatography (enantio×polar) with time-of-flight mass spectrometry to determine chiral lactones and characterize the volatilome of Marsala wines

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Abstract

The present research is focused on the targeted determination of fifteen chiral lactones along with the untargeted characterization of the volatile fraction of Marsala wines (a dessert wine), by using headspace solid-phase microextraction coupled to flow-modulated comprehensive two-dimensional gas chromatography (enantio column×polar column) with time-of- flight mass spectrometry and hydrogen as carrier gas. Among volatile compounds, lactones, particularly γ- and δ-, are important constituents of food and beverage aromas and may be markers of alcoholic beverage aged in wood barrels and aroma adulteration. In such a respect, and considering important aspects related to food authenticity, their determination can provide information on such aging processes. The proposed analytical method aims to meet this goal analysing ten types of Marsala wines. Finally, targeted lactones were quantified by constructing matrix-matched calibration curves, with both limits of detection and instrumental detection limits calculated. Furthermore, emphasis was devoted to the investigation of Marsala wine volatilome, highlighting the highly complex nature of its headspace, with over 300 compounds tentatively identified.

L-14

Linear and radial HPTLC coupled with high resolution mass spectrometry imaging

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Abstract

HPTLC is a separation method that can be used for rapid screening of lipids. The coupling with HR MALDI mass spectrometry imaging allows their identification and semi-quantification using internal standards. HPTLC can be performed as a linear or radial separation that are compared. The major parameters for method optimisation have been studied and are summarized. The transfer towards lower resolution routine instruments is possible but MALDI conditions such as matrix deposition and laser settings should be strictly controlled. Data handling is facilitated by Kendrick mass defect filtering. The application of the method to biological such dried droplets blood samples and food samples will be presented. A large panel of applications can be foreseen when molecular identification is required.

L-15

Mineral oil analysis in food: an analytical challenge

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Abstract

Mineral oil can enter the food chain in many different ways: (i) as a contaminant via e.g., environment or lubricants used in equipment or machinery, (ii) as an additive or technical auxiliary or (iii) as a residue via the migration from materials and objects that come into contact with foodstuffs. The analysis is very challenging since mineral oil is a very complex mixture. Among the many different substances present in mineral oil, two main types can be distinguished: the saturated hydrocarbons (MOSH) comprising a complex mixture of linear, branched and cyclic compounds and variable amounts of aromatic hydrocarbons (MOAH). Both MOSH and MOAH form “humps” of unresolved peaks in the chromatograms with the same range of volatility. Since these two fractions have a different toxicological relevance, it is important to quantify them separately.

Commonly, an on-line technique existing of a combination of Liquid Chromatography with Gas Ghromatography (LC-GC) with Flame Ionization Detection (FID) is used for quantification of MOSH and MOAH. The tested matrix has an important impact, not only on data integration and interpretation but also on the sample preparation. Due to the presence of olefins and natural alkanes, some matrices require auxiliary methods such as epoxidation and clean-up with aluminium oxide. An overview of how to deal with this challenging analysis for different type of matrices will be presented.

L-16

Application of multi analytical chromatography platforms and chemometric processing for the phytochemical profiling of *Cannabis sativa* inflorescences

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Abstract

Cannabis (*Cannabis sativa* L.), also known as hemp, is one of the earliest cultivated crops, grown for both the use of fibres in textile and cordage production, and its unique chemical properties. However, due to the restrictions on the legal requirements regulating cannabis cultivation, it is not a well characterized plant. Only recently regulatory bodies are beginning to ease enough to allow more breath toward cannabis research activity, which, coupled with the pharmaceutical industrial interest is fuelling the interest of the scientific community. Many factors influence the phytochemical profile of cannabis inflorescences including variety, growth area, processing conditions and post-harvest storage. Within this study, the potential of comprehensive two-dimensional (2D) gas chromatography (GC×GC) mass spectrometry combined with novel chemometric data processing is demonstrated. Furthermore, the profiling of Cannabinoids and efficacy of potency testing via liquid chromatography is shown. The comprehensive chromatographic data of floral aroma were aligned and compared using a tile-based approach followed by data mining to gain extra-layers of information. Hierarchical clustering and multivariate statistical approaches were used to correlate chemical similar samples, and promising discriminatory marker features were found. Based on both floral aroma and cannabinoid analysis results, it was possible to discriminate across varieties and storage conditions and within the same variety differences were shown in relation to growth area. The variability in aroma profile and cannabinoid composition shown through the presented analytical workflow can provide a potential tool for an in-depth characterization of Cannabis phytochemicals for the pharmaceutical and cosmeceutical industry and help in producers the selection of varieties less susceptible to changes in aroma and cannabinoid content due to storage conditions. Furthermore, the application of multi analytical platforms increases precision in aroma interpretation and potency testing, enabling improved product labelling.

L-17

Challenges of choosing a different carrier gas in GC/MS: Hydrogen or Nitrogen?

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Abstract

In GC/MS mostly helium is used as the carrier gas. The challenge with helium is that it is expensive and will only become more expensive. Also, the supply is not secured which makes many labs look for alternatives. It is possible to use nitrogen or hydrogen as the carrier gas in GC/MS. Big advantage of these gases is their low cost and secured availability. They can even be produced in the lab. Depending on the separations required it is possible to use nitrogen or hydrogen. Nitrogen has been shown to be well usable in MS using APCI. A 20m x 0.15mm capillary under N2 will show exact the same efficiency as a 30m x 0.25mm under Helium. Nitrogen and EI Ionization typically results in a big loss of sensitivity.

Hydrogen can also be used in a MS, but there are a few challenges related to flows, fragmentation, reactivity of ion source and hydrocarbon background which all will be discussed in this presentation

L-18

A new greener way for aflatoxins determination in pistachio: a deep eutectic solvent–based approach

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Abstract

Since their discovery in the 60' aflatoxins have posed a serious issue on public health and a challenging target for food quality control. Indeed, their carcinogenic potential and presence in different food matrices (nuts, maize, rice, and dairy products) led authorities to set maximum levels of these contaminants. Due to their slightly polar nature, official methods are based on methanol/water or acetonitrile/water solutions as extraction media. Pistachios samples are complex, rich in interferents compounds; hence a sample preparation step is crucial prior analysis. Here, a new method based on deep eutectic solvents (DES) as extraction media is proposed. DESs are a new class of green solvents based on coupling a hydrogen bonding donor and a hydrogen-bonding acceptor in an appropriate molar ratio. Most DESs already showed not toxic and biodegradable properties with good extraction power for several compounds. Due to the complex nature of the extract, a further clean-up and concentration step was mandatory. DES extracts were diluted with water and passed throughout a Supelco Discovery® DSC-18 SPE cartridge, the trapped aflatoxins were then eluted with a minimum quantity of methanol and injected on HPLC-FLD equipped with a partially porous Supelco Ascentis Express® C18 column used in ultra-HPLC conditions. The mobile phase was composed of methanol and water under gradient elution conditions: from 30% to 60% MeOH in 7.5 min. The flow rate was 0.45 mL/min, the injection volume was 2 µL and the temperature of the column maintained at 35°C. This approach showed the feasibility of DES as extraction media for such a complex matrix, reducing the use of typical solvents and process waste.

L-19

Micro thermal desorption as a sample introduction to hyper-fast GC

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Abstract

The hyper-fast thermal gradient GC is particularly suitable for the measurement of thermally labile substances. The reason is the strongly lowered analysis temperature, which prevent substances from decomposing during chromatography. This is especially the case for explosives.
In order to obtain low detection limits, thermal desorption (purge and trap) is a suitable method. In forensic use, low concentrations of the target substances must be collected and enriched. This has also been done so far with classical thermal desorption. However, the procedure is time-consuming because the standardised thermal desorption tubes are large in volume and have a high thermal mass. Heating the tubes and thus releasing the enriched substances takes some minutes. In addition, a further stage of focusing is often required to obtain a narrow band when the substance is applied to the separation column.

In the lecture, a new method of micro thermal desorption will be presented. The tubes are only 1/16" in diameter and very thin-walled. In a special open injector, the tubes are heated very quickly and release the substances. The substance bands are therefore narrow. An optional cold spot directly at the head of the resistively heated separation column is sufficient for focusing, which makes the technical complexity very low.

Measurements of a wide range of explosives are presented, additionally also measurements of warfare agent simulants.

L-20

Coupling capillary electrophoresis with ion mobility mass spectrometry: Choose your own orthogonality for experimental physical chemistry or analytical chemistry applications

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Abstract

CE is an alternative to chromatography where ionizable compounds are resolved by size and charges. Capillary electrophoresis (CE) and ion mobility spectrometry (IMS) are both electrophoretic methods separating ions submitted to an electric field. The first is occurring in solution (averaged charges) while the second is operating in the gas phase (electrospray charge state distribution). IMS is ideally coupled to mass spectrometry (IM-MS). It allows collision unfolding a low internal energy uptake and fragmentation at higher collision energy additionally to mass detection.

CE coupled to IM-MS offers broad fields of application going from the separation, quantitation, and identification of low molecular weight compounds to small or large (bio)polymers sequencing, molecular weight determination, or polydispersity.

The ion mobility coefficient obtained from IMS can be converted into collision cross section (CCS), which describes the global shape of the ions. The CCS is also used as an ion descriptor for analytical applications. The electrophoretic mobility (μ_e) obtained from CE acts like the alter ego of the CCS but in solution.

The experimental μ_e and CCS could be compared with atomic coordinates of candidate structures obtained from database (such as the RCSB PDB databank) or from computational chemistry such as Density Functional Theory or Molecular Mechanics/Dynamics. Theoretical μ_e and CCS are computed and compared with experimental data. Folding information of (supra)molecular systems or assemblies and their dynamics can be derived from the CE, IM-MS, and theory. The coupling of CE and IM-MS provides useful insight about the global shape of ions before and after desolvation.

Additionally (bio)polymer and compounds containing repeating units (as described by Kendrick) can be plotted as trends of the μ_e or CCS as function of mass-to-charge ratio (m/z), or Kendrick mass, describing how the global shape of the ions evolves with the mass.

L-21

The versatility of high-resolution separation techniques for targeted and non-targeted analysis

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Abstract

Classical targeted analysis aims at quantifying one of some well-known analytes in the sample, considering the remaining chemical domains as interference and superfluous. In doing this, the entire analytical workflow, from the sample preparation to the data elaboration, is selectively optimized towards the defined analyte.

However, advances in multidimensional gas chromatography, mass spectrometry and high-throughput data processing capabilities have instigated a paradigm shift in molecular analysis over the past decades [1-2]. Their combo makes up a final hyphenated high-resolution technique, allowing the separation and monitoring of many more analytes and chemical domains in the samples. This idea of non-targeted analysis is the driving approach of the modern omics sciences for the discovery and understanding of complex systems.

The presentation will showcase examples of targeted and non-targeted analysis exploiting comprehensive two-dimensional gas chromatography coupled to mass spectrometry (GC×GC-MS) over a wide range of applications [3-6].

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L-22

Column design, quantitative assessment of the 3D pore space, and performance characterization of polymer monolithic capillary columns targeting high-resolution peptide profiling

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Abstract

Polymer monolithic stationary phases have emerged as a good alternative for packed column formats. To increase the resolving power of packed bed columns, the particle size can be optimized. However, downscaling the particle size leads to increase in pressure proportional to the fourth power. The porous structure of polymer monoliths can be to some extent optimized such that macropore size and globule size are tuned independently. By simultaneously tuning phase ratio, microglobule sizes and macropore sizes, here we report a highly repeatable poly(styrene-co-divinylbenzene) capillary monolithic column fabrication approach to further push forward the kinetic performance of the state-of-art polymer monolithic column. Serial block-face electron microscopy was applied for three dimensional and quantitative characterization of column bed morphology. The optimized columns have been characterized both morphologically and chromatographically, producing a separation impedance of 924 (reduced by 10-fold of the commercial monolith column as benchmark). The column-to-column repeatability has been demonstrated by comparing 12 columns made from different batches in different days, resulting RSDs of 6.7%, 1.5% and 3.2% for peak width, retention time and back pressure normalized by length, respectively.

L-23

Colorectal Cancer Diagnostic Biomarkers Screening: Multi-modal Metabolomics & Lipidomics Approach

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Abstract

Colorectal Cancer (CRC) is the third most diagnosed cancer, leading to the second highest number of cancer-related deaths with poor prognosis. The current screening methods for CRC are either highly invasive, such as colonoscopy, or lack sufficient sensitivity, such as the Fecal Occult Blood Test (gFOBT) and Immunochemical FOBT (FIT).

Therefore, the aim of the research is to identify sensitive and less invasive diagnostic biomarkers for CRC by utilizing a comprehensive two-dimensional gas chromatography (GC×GC) technique coupled with low- and high-resolution time-of-flight mass spectrometry (TOFMS).

We conducted a study on 64 human serum samples representing three groups (Adenocarcinoma (ADK), Adenoma, and Control) using GC×GC–TOFMS. We analyzed samples with two different statistically tailored sample preparation and analytical approaches for metabolomics (50 µL serum) and lipidomics (fatty acids) (25 µL serum). All serum samples were injected in a randomized order along with a QC sample (pooled human plasma) and NIST SRM 1950 to fulfill QAQC requirements.

Advanced statistical analysis using supervised and unsupervised methods and analysis of metabolic pathways were employed on both datasets. Results from the lipidomics study revealed that certain omega-3 polyunsaturated fatty acids (PUFAs) were inversely associated with an increased likelihood of CRC, while some omega-6 PUFAs showed a positive correlation. Meanwhile, the metabolomics approach found dysregulation of certain proteogenic amino acids (Ala, Glu, Met, Thp, Tyr, Val), Myo-inositol, and 3-hydroxybutyric acid in CRC. This unique research provides a more comprehensive understanding of the molecular-level changes associated with CRC. It enables a comparison of the effectiveness of two distinct analytical approaches for CRC screening using the same serum samples and single instrumentation.

Poster

P-01

Aroma profiling of chocolate: How do plant-based and low sugar varieties compare to regular milk chocolate?

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Abstract

Environmental and dietary concerns are driving a change in the chocolate industry. 'Low sugar' chocolate is increasing in popularity, as consumers are becoming more health-conscious and seeking alternatives to traditional confectionary, while plant-based chocolate caters to consumers who are looking for vegan or vegetarian options, as well as those concerned about the environmental impact of animal agriculture.

However, the challenge for confectioners is to ensure that the depth of flavour is maintained. Aroma profiling by GC–MS is often used to characterise the chemical composition of chocolate and its sensory properties – with a wide range of aroma-active compounds already identified, such as aldehydes, ketones, esters, and pyrazines.

Typically, headspace sampling or solid phase microextraction (SPME) is performed to capture the volatiles for analysis by GC–MS, but these techniques are often limited in sensitivity. Additionally, such complex aroma profiles can prove difficult to separate using conventional GC–MS.

Here, we demonstrate the use of high-capacity sorptive extraction with novel trap-based focusing for enhanced sensitivity and improved chromatographic performance. We couple this with improved separation by comprehensive two-dimensional gas chromatography and time-of-flight mass spectrometry (GC×GC–TOF MS) for greater detail on the composition of chocolate aroma.

This technique has the potential to provide valuable insights into the factors that influence the aroma of chocolate, which can be useful when engineering new chocolate products with specific aroma characteristics. However, sampling, separation and detection is just the beginning – the resulting datasets must then be reduced to discover significant differences and allow meaningful conclusions to be drawn. Here, we apply easy-to-use chemometrics software to automatically align and compare the complex chromatograms, for fast identification of key differentiators.

We will show this efficient end-to-end workflow in action for the comparison of aroma profiles from various milk chocolate bars, including 'low sugar' and 'plant-based' varieties.

P-02

Utilization of Stir Bar Sorptive Extraction - Gas Chromatography - Mass Spectroscopy Technique to Study the Aroma Active Compound Production during Kombucha Fermentation

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Abstract

Since the sensorial profile is the cornerstone for the development of kombucha as a mass market beverage, advanced analytical tools are needed to gain a better understanding of the aromatic compounds' kinetics during the fermentation to control the sensory profiles of the drink. The volatile organic compound (VOCs) kinetics were determined by stir bar sorptive extraction – gas chromatography – mass spectrometry and odor-active compounds were considered to estimate consumer perception. A total of 87 VOCs were detected in kombucha during the fermentation stages. The synthesis of phenethyl alcohol and isoamyl alcohol probably by Saccharomyces genus principally, led to esters formation. Moreover, the terpene synthesis occurring at the beginning of fermentation (Δ-3-carene, α-phellandrene, γ-terpinene, m- and p-cymene) could be related to yeast activity as well. Principal component analysis spotted classes that allowed the major variability explanation, which are carboxylic acids, alcohols, and terpenes. The aromatic analysis accounted for 17 aroma-active compounds. These changes in the evolution of VOCs led to flavor variations: from citrus-floral-sweet notes (geraniol and linalool domination), fermentation brought intense citrus-herbal-lavender-bergamot notes (α-farnesene). Finally, sweet-floral-bready-honey notes dominated the kombucha flavor (2-phenylethanol). As this study allowed to estimate kombucha sensory profiles, an insight for the development of new drinks by controlling fermentation process was suggested. Such methodology should allow a better control and optimization of their sensory profile, which could in turn lead to greater consumer acceptance.

P-03

Development of a workflow for the characterization of pyrolysis oils from plastic waste using multidimensional gas chromatography and mass spectrometry

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Abstract

Plastic is one of the most widely used materials in the world. From 2016 to 2020 an increase of production of virgin plastic was observed in the world, from 335 to 367 Mt [1], but only 9% of its waste was recycled correctly in 2019 [2]. In Europe these data are most optimistic: the production of plastic was decreased during the same five years (from 60 to 55 Mt, with a maximum of 64.4 Mt in 2017) and the post-consumer waste trend shows an increase of 117.7% and -46.4% in recycling and landfill, respectively [1].

Among the type of recycling there is the chemical recycling through which pyrolysis oils are produced. These oils can be used as biofuel and to produce new plastic materials, thereby reducing the environmental impact of plastic waste and showing high potential for sustainable and green energy challenges.

In this contribution, a preliminary workflow is presented for the characterization of pyrolysis oils, in terms of heteroatom-containing compounds and hydrocarbons' classes. The samples are just diluted before being analyzed in comprehensive two-dimensional gas chromatography with mass spectrometry (GC×GC-MS). Pyrolysis oils are mainly constituted by hydrocarbons, which have been divided into the various classes (PIONA) by exploiting the high structure organization of chromatograms obtained by GC×GC. Moreover, in these samples there are different O-, N-, S-, Cl-containing compounds, that have been identified by the peculiar mass fingerprints and elution locations.

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P-04

Exploiting sorbent-based sampling and single-stage thermal desorption coupled to comprehensive two-dimensional gas chromatography to profile the scent of floral parts from Cannabaceae species

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Abstract

The floral smell is an important phenotypic characteristic of flowering plants, and it plays a critical role in attracting pollinators to enable reproduction success. In some cases, it can also protect plants from insect and animal damages.

The floral scent derives from the presence of volatile secondary metabolites, which contains various low molecular weight compounds with a low boiling point. They are mainly synthesized via the terpenoid, benzenoid, and fatty acid biosynthetic pathways. These volatile compounds have been widely used in cosmetics, medicinal products, perfumes, and food flavourings.

Terpenoids are the main responsible for the aroma of many flowering plants, including the those belonging to the Cannabaceae family.

Among the Cannabaceae, the most famous species are represented by Cannabis (hemp), Humulus (hops), and Celtis (hackberries).

The present contribution aims at exploring, in a detailed manner, the volatile composition of different Cannabaceae plants/species, using state of the art comprehensive two-dimensional gas chromatography coupled to mass spectrometry (GC×GC-MS) technology. The head-space extraction was based on dynamic and sorbent-based approach, and specifically using trap tubes, packed with solid sorbent material which were properly selected for the terpenoids affinity. After the extraction, they were thermally desorbed online with the GC×GC-MS system. Identification of the volatile compounds was carried out using mass spectral similarity and retention indices.

P-05

Aroma Compounds in Balsamic Vinegars: Optimization of Headspace Solid-Phase Microextraction (HS-SPME) for Multidimensional Gas Chromatography coupled with Mass Spectrometry (GC×GC-MS) Analysis

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Abstract

Balsamic vinegar is one of the best known and most popular types of Italian vinegar in the world. In Italy, precisely in Emilia Romagna, PDO and PGI balsamic vinegars are produced exclusively in the provinces of Modena and Reggio Emilia and with specific varieties of grapes grown for this purpose. In fact, there is a European specification for the production of these food products in order to preserve their tradition and origin.

The aroma, and therefore the typical balsamic flavor of this product, is a very important food characteristic, determined by the presence of hundreds of volatile compounds belonging to different chemical families. The characterization and understanding of the main aromatic compounds present are therefore of great importance in defining the quality of balsamic vinegar.

In this contribution, headspace solid-phase microextraction was applied for the analysis of aromatic compounds in vinegar. This rapid and inexpensive sample preparation method is often used in combination with GC-MS for the extraction of volatile compounds from a wide variety of different samples.

Some of the parameters that most influence extraction, including fiber type, salt concentration and sample volume, were optimized using a chemometric approach based on the use of an optimal set of experiments (experimental design).

This allowed us to optimize the effects of extraction on the sample matrix and thus to define the conditions for the separation and detection of aromatic compounds in balsamic vinegar by exploiting multidimensional gas chromatography coupled with mass spectrometry (GC×GC-MS). This made it possible to obtain detailed fingerprinting of the aromatic compounds present and to define the complex organoleptic profile of these high-value products.

P-06

Evaluation of volatile compounds in cocoa beans (*Theobroma cacao* L.1753) from new fermentation media in Ivory Coast

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Abstract

Fermentation of cocoa beans (*Theobroma cacao* L.) is an essential step in the post-harvest cocoa process. It will influence the market and organoleptic quality of the beans and derived products. It should be noted that this major process in the transformation of cocoa is nowadays carried out using various techniques by producers in Côte d'Ivoire. Based on a field survey, several reasons have been identified. It appears that palm leaves, cocoa pods, tarpaulins, polypropylene bags and jute bags are respectively the most frequently used. The objective of this study was to determine the volatile organic compounds profiles (VOCs) of beans obtained after fermentation realized on conventional and innovative media. For the identification of VOCs, solid phase micro-extraction and gas chromatography-mass spectrometry (SPME-GC-MS) were performed. In total, 27 compounds with a corresponding percentage higher than 80% were detected in cocoa powders without prior roasting. Only three of them were common to all experimental fermentation media. The results revealed that pyrazines typically described with a sweet chocolate flavor and thus positively influencing aroma, were detected only in beans fermented on palm leaves, bags, polypropylene sheets and in jute bags. These carriers are therefore likely to produce better flavoured chocolates than the banana leaves usually recommended.

Keywords: Cocoa, *Thebroma cacao* L., Volatile organic compounds, SPME-GC-MS, Fermentation.

P-07

Enhanced analyte extraction with automated multi-phase high-capacity sorptive extraction (HiSorb) for GC-MS

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Abstract

The use of high-capacity sorptive extraction techniques are increasing amongst analysts, to enhance the extraction of volatile organic compounds (VOCs) from a range of sample types, including foods, beverages, environmental water and soil, and more recently in clinical research and development applications. Until now, commercially-available extraction phases have been limited to a rather narrow range of chemical sorbents, dominated in popularity by the 100% poly(dimethylsiloxane) (PDMS) sorbent phase, a polyacrylate (PA) phase and a hybrid offering with PDMS as copolymer to a more polar yet temperature-sensitive semi-solid of polyethylene glycol (PEG). Due to this, desorption temperatures are restricted for these polar phases, often leading to inefficient release of analytes (that need higher temperatures) from the phase and into the analytical system, resulting in carryover on the phase in subsequent analyses.

The technique provides a solvent-free approach with few sample preparation steps compared to conventional techniques, such as liquid-liquid extraction (LLE), however, the sample extraction process remains quite manual, with the analyst having to insert the extraction device (supporting the extraction phase) into the sample vial and, after extraction has finished, removing, washing and drying the device, before transfer to an instrument for analysis.

Here, we present the evaluation of new phases intended to extend the applicability of high-capacity sorptive extractions for VOCs to cover a wider volatility range in a fully-automated workflow, from sample extraction, through to washing, drying and injection of analytes, for gas chromatography-mass spectrometry (GC-MS) analysis. As well as enhancing VOC extraction, there are few demands placed on the analyst, enabling high, unattended sample throughput, and faster reporting of results.

P-08

A Novel EI Source Optimized for Use with Hydrogen Carrier Gas in GC/MS and GC/MS/MS

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Abstract

Recent concerns with the price and availability of helium have led laboratories to look for alternative carrier gases for their GC/MS and GC/MS/MS systems. Among the problems encountered when converting to hydrogen carrier gas in GC/MS is that hydrogen is a reactive gas and may cause chemical reactions in the mass spectrometer electron ionization (EI) source. This can lead to disturbed ion ratios in the mass spectrum, spectral infidelity, and peak tailing. This presentation will discuss a novel EI source developed to address hydrogen-related issues in the EI source enabling improved performance with hydrogen carrier gas in GC/MS analysis. The benefits of using the novel EI source will be discussed for several GC/MS applications.

P-09

Antiplasmodial-guided investigation of *Lantana camara* (Verbenaceae)

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Abstract

Background: Despite great efforts to control and eliminate malaria, it is still one of the major causes of death and poverty in Africa. An inventory of traditional plants used in Cameroonian folk medicine in the treatment of malaria was carried out by means of in-depth bibliographic studies and ethnopharmacological field surveys in the west region of Cameroon. This survey revealed that, *Lantana camara* is locally used to cure malaria and many other diseases. This work reports the phytochemical study and the results of the evaluation of the antiplasmodial activities on *Plasmodium falciparum* $3D_7$ and Dd_2 strains carried out on *Lantana camara*.

Results: From ethanolic extract of the leaves and the ethyl acetate – methanol (12:13, *v/v*) extract of roots, 18 compounds were isolated using usual chromatographic methods including 08 triterpenoids, 03 flavonoids, 01 chlorophyll, 04 steroids, and 02 furanonaphthoquinones.

The ethanolic extract of leaves exhibited a good activity against the $3D_7$ and Dd_2 strains with IC_{50s} values of 14.31 and 35.95 µg/mL respectively and the ethyl acetate – methanol (12:13, *v/v*) extract of roots exhibited a good activity against the $3D_7$ and Dd_2 strains with IC_{50s} of 11.36 and 18.07µg/mL, respectively. The fraction FB of roots extract showed a high activity against Dd_2 with an IC_{50} of 7.73 µg/mL. From this fraction, diodantuzenone and isodiodantunezone (2:1) were isolated which exhibited a high potential against Dd_2 with an IC_{50} of 6.07µM (IC_{50}=0.04µM for Artemisinin). To the best of our knowledge, our work reports for the first time the strong antiplasmodial potential of diodantuzenone and isodiodantunezone against the strain used.

Conclusion: These results confirm the uses of *Lantana camara* in traditional medicine to cure malaria.

Impact of the study: Our work could contribute to improving the living conditions of populations through the design of Improved Traditional Medicines (MTA).

Keywords: *Lantana camara*; Antiplasmodial assay; Furanonaphthoquinones.

P-10

Understanding consumer preference of hard seltzer drinks using advanced analytical tools with sensory data correlation

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Abstract

Seltzers (also known as soda or soft drinks) have a global market value of over US$400 billion which is expected to reach over US$600 billion by 2030. In addition to popular non-alcoholic products, such as cola and lemonade, the hard seltzer market has grown substantially over the past two years, offering low-calorie, zero carbohydrate, alcoholic beverages as healthier alternatives, while also being vegan and gluten-free. With over 200 new brands in the competitive market, understanding consumer preference is vital to ensure longevity in the market.

Sensory evaluations are typically performed to understand consumer preference which is important for brands to remain competitive and develop new products. Consumers are given anonymised products and asked to record their assessment of smell, taste, look and touch. However, results are highly subjective, and the compounds responsible for the aroma are not identified.

Analytical techniques like headspace and SPME have previously been employed to sample the aroma- and flavour-active volatile organic compounds (VOCs) from products such as beverages. Results are used alongside sensory evaluations, enabling better decision-making and quality control. However, these techniques can often be limited in terms of sensitivity and chromatographic performance. Here, we evaluate the use of sorptive extraction (HiSorb) probes for immersive sampling of seltzers, using a range of different sorptive phases. This technique offers a higher capacity of sorptive phase compared to traditional SPME, enabling higher sample loadings which, in conjunction with secondary refocusing, offers excellent sensitivity for a wide range of chemical classes from VOCs to SVOCs, and improved chromatographic performance. The technique allows maximum sample detail to be obtained, with analysis by thermal desorption (TD)–GC–MS. We will then show how data mining and multivariate statistical analysis of the complex aroma profiles can determine brand differences and correlate this to sensory data to understand consumer preference.

P-11

Application of 2D-LC with MS Detection with Superficially Porous Columns to the Analysis of Cold Medicine

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Abstract

Ion pair chromatography is commonly used for the analysis of polar compounds in compendial methods or as referee methods. Unfortunately, ion-pair reagents lead to ion suppression and reduce the ionization efficiency needed to identify impurities by LC/MS. Superficially porous particle LC columns are a popular tool in liquid chromatography. Superficially porous particle columns generate high efficiency at lower pressure, relative to their totally porous particle column counterparts, which is a benefit for impurity analysis. In this work, the multi heart cutting valve and 2D-LC system is used to extract and identify several OTC cold medication components after initial separation using reversed phase ion pair chromatography and single quad mass spectrometry.

P-12

Comparison of different sample preparation protocols for high-sensitivity determination of polycyclic aromatic hydrocarbons (PAHs) in vegetable oils

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are environmental and processing contaminants that can contaminate vegetable oils through different routes. They are compounds with 2-6 fused aromatic rings, mainly originated by incomplete combustion of organic matter at high temperature.

Due to the demonstrated carcinogenic and genotoxic potential of heavy PAHs (3-6 benzene rings), Commission Regulation (EC) No. 835/2011 set maximum legal limits for benzo[a]pyrene and the sum of 4 heavy PAHs (PAH4) in vegetable oils and other food items. Due to their lipophilic character, vegetable oils may be highly contaminated with PAHs. Most of the works in the literature investigated on PAH4 and PAH8 as better indicators based on occurrence and toxicity data (1). The determination of PAHs in vegetable oil is complicated by the presence of a huge amount of triglycerides, and several methods have been proposed in the literature to remove them before analytical determination (1-2). Therefore, the aim of this study was to find a fast and low-solvent consumption method to selectively isolate PAHs from vegetable oils before analytical determination. For this purpose, MAS (microwave-assisted extraction) and low-temperature fat precipitation, both followed by a rapid SPE cleanup, were compared. Both these sample preparation techniques allowed to reach good sample enrichment and hence high sensitivity and utilize a low amount of solvent. Both of these sample preparation techniques resulted in good sample enrichment and thus high sensitivity, using a low amount of solvent. The suitability of the proposed sample preparation protocols was evaluated using both ultra-high performance liquid chromatography (UHPLC) and gas chromatography-mass spectrometry (GC-MS) with single ion monitoring (SIM).

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P-13

Analytical and validation strategy for the determination of acrylamide in a wide variety of foodstuffs

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Abstract

Acrylamide is a food processing contaminant classified as a probable carcinogen. Since its discovery in 2002, it has been intensively studied in very specific food commodities (i.e., fries, crisps, coffee). However, as acrylamide is formed from asparagine and sugars precursors during a heating process, it can be potentially present in any cereal-based or tuber-based foods. Based on this information, the European Commission published the Recommendation 2019/1888 to monitor the presence of acrylamide in various foods (i.e., potatoes/vegetables-based food, coffee substitutes, composite dishes, olives, dried fruits). This poster highlights how to deal with this huge food variety without spending tremendous time in analytical development and validation.

The strategy elaborated was to use a QuEChERS extraction for all foods, followed by a specific clean-up depending on the proportion of proteins/fats/sugars/water in the food. Food samples have been divided into four groups; a specific balance of C18 and PSA d-SPE sorbents have been used for each. Due to interfering peaks during the chromatography, coffee and cocoa powders had to follow an alternative method based on water extraction, followed by purification on a multimode SPE cartridge. Validation was done for each of the five groups, and different food items were used to represent each food group's diversity better.

This strategy allowed the validation of the acrylamide method in a wide variety of food commodities in a short period of time. All EU regulation 2017/2158 validation criteria were met (75-110% recovery and RSD ≤ 22%). A low LOQ of 20 µg kg-1 has been reached for the five food groups, and the method has been successfully applied to the analysis of 250 market samples, answering at the same time to the call of the Commission Recommendation (EU) 2019/1888.

P-14

Fungal volatile organic compounds: new targets for the detection of fungal contamination and mycotoxin production

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Abstract

Fungal volatile organic compounds (fVOCs) are secondary metabolites released by filamentous fungal species including those belonging to the mycotoxigenic genera such as Aspergillus, Fusarium and Penicillium. These widespread fungi can contaminate foodstuffs at various stages of cultivation and storage. In the meantime, these fungi can also produce mycotoxins, which are highly toxic molecules at low concentrations to all vertebrates, including humans. One of the most abundant mycotoxins is aflatoxin B1. This mycotoxin can induce serious illness (chronic exposure) and death (acute exposure). Current detection methods of these mycotoxins consist in analyzing samples previously extracted from a batch using ELISA or HPLC tests.

A relation between these two types of secondary metabolites, fVOCs and mycotoxins, has been suggested in previous works. This work gathers the results obtained in several experiments generated by two of the most frequent and harmful fungi in contaminating food commodities, Aspergillus flavus and Fusarium verticillioides.

SPME fibers were used to extract the fVOCs, followed by a separation by gas chromatography and their identification by mass spectrometry.

The aim of this study was to evaluate the impact of experimental conditions on fVOC emission and mycotoxin production (aflatoxins and fumonisins). The following parameters were studied: culture substrate, temperature and, fungal growth conditions (growing alone, co-culture, under special atmosphere). Finally, the sampling and semi-quantification of fVOCS was optimized in a view to use fVOCs as marker of fungal contamination and mycotoxin production.

P-15

Study of the formation of perfluoroalkyl carboxylic acid (PFCA) dimers in gas phase by coupling ion mobility with mass spectrometry (IM-MS)

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Abstract

Per- and polyfluoroalkyl substances (PFASs) are emerging pollutants of great concern, with over 5,000 compounds currently reported. Non-targeted analyses of these substances by liquid chromatography (LC) coupled to high-resolution mass spectrometry (HRMS) remain challenging due to the possible presence of numerous isobars and isomers, and the low number of available analytical standards. In this regard, the coupling of ion mobility spectrometry (IMS) to conventional LC-HMRS offers new perspectives for PFAS analysis due to the additional IMS separation dimension. Furthermore, the structural descriptor obtained from the collision cross-section (CCS) that can be calculated from the measured ion mobility provides an additional identification parameter. In addition, CCS-m/z trends are observed for compounds with repeating units, such as polymers or PFASs, and can increase confidence in identifying of homologs. When trapped IMS (TIMS) is coupled to LC-MS to analyze legacy perfluoroalkyl carboxylic acids (PFCAs), multiple mobility peaks are observed at the *m/z* of a single deprotonated ion, preventing the determination of an unambiguous CCS as an identifier. Of the peaks detected in the mobilogram of a deprotonated PFCA ion, the one with the lowest CCS was confidently assigned to the deprotonated PFCA ion in its monomeric form. The peak with the highest CCS was assigned to a homodimeric PFCA ion ([2M-H] -) that existed prior to ion mobility separation and could dissociated after mobility separation. The CCS-*m/z* trendlines of the monomeric and dimeric PFCA ions were obtained using three different ion mobility instruments: drift tube, traveling wave and trapped ion mobility spectrometers (DTIMS, TWIMS and TIMS) and compared. If there is any difference in ion heating during ion mobility separation (Morsa *et al*., Anal. Chem. 2011 83(14):5775-5782) between the three IMS instruments mentioned, this should influence the overall shape of the dimers, leading to different CCS-*m/z* trends.

P-16

Stability study of multiple pesticides in passive silicon wristband samplers over time at room temperature and at - 20°C in a potato cultivation context

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Abstract

Potato is one of the most important staple crops in the world, making potatoes a key crop for improving food security. As a result, there has been growing interest in sustainable and environmentally friendly methods of potato cultivation. In the IMPOCHA project, the main objective includes an assessment of the exposure of Chinese and Belgian farmers and their families to pesticides used on potato crops through a silicone wristband. This presentation highlights the pesticide stability study in the wristband over time, which evaluated the possible loss of pesticide residues during the transit from the Chinese farm to the Belgian laboratory. A list of 70 pesticides of interest has been established based on Belgium's authorized plant protection products for potato crops. An analytical method to quantify pesticides in the wristband was developed based on acetone extraction followed by solvent exchange with acetonitrile and purification with d-SPE C18 sorbent. Analysis was performed using LC combined with mass spectrometry. The method was validated according to SANTE/11312/2021 criteria and is fit for assessing pesticide stability in the wristband. Most pesticides are validated at 1 ng/g per wristband.Pesticide stability was assessed at room temperature and at -20°C for 15 days by first cleaning silicone wristbands and then spiking them with a solution containing all the selected pesticides.The stability study enables a comprehensive overview of pesticide losses during transit and advises the best transport conditions and the appropriate time between the experiment and wristband analysis.Discussion with partners allowed us to establish the most realistic scenarios taking into account storage by the participant and transit from the participant to the Belgian laboratory. The experimental wristbands should be stored at -20°C on the farm, during transportation and in the laboratory, as the transit time is challenging to assess, and partners have no hold over it.

P-17

Fractionation of rosemary solid residue from steam distillation: the relationship between phenolic profile and biological activities

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Abstract

Chromatography is a significant biophysical method for separating, identifying, and purifying the constituents of a mixture. Our work aims to study the effect of fractionation of rosemary solid residue remaining after steam distillation on biological activities and their relationship with the chemical profile. Nine fractions were obtained by silica gel column chromatography. Identification of the separated molecules was carried out by high-performance liquid chromatography-photodiode array detector (HPLC-DAD) and gas chromatography-mass spectrometry (GC-MS). The Antioxidant activity was established using DPPH, and the enzyme tyrosinase was used to assess anti-tyrosinase activity. In addition, antimicrobial capacity was studied against *Escherichia coli* ATCC 25922 and *Listeria innocua* ATCC 33090, two well-known organisms representing gram-negative and gram-positive bacteria respectively, as well as against the mold *Geotrichum.s p* and the yeast *Rhodotorula glutinis*.

Keywords: Rosemary, Steam distillation, Column chromatography, HPLC-DAD, GC-MS, Biological activities.

P-18

Sliding windows in ion mobility (SWIM): a new approach to increase the separation power in trapped ion mobility-mass spectrometry hyphenated with chromatography

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Abstract

Ion mobility spectrometry (IMS) coupled to mass spectrometry is a promising and powerful tool for the analysis of small organic molecules in complex samples. In recent years, the separation capability of commercially available IMS instruments (e.g., TIMS, cTWIMS and SLIM) has improved drastically. However, achieving such high resolving power typically requires extended measurement times or analysis of ions over a restricted ion mobility range, which can pose significant challenges when coupling the IMS-MS instrument with front-end chromatography and analyzing compounds displaying a wide range of collision cross section (CCS) values.

We have developed a novel approach for improving the resolving power of trapped ion mobility spectrometry (TIMS) when coupled with gas chromatography, called "Sliding Windows in Ion Mobility" (SWIM). Contrary to the standard TIMS mode which employs a broad and constant IM analysis range, the SWIM mode uses narrow and mobile ion mobility windows that are continuously scanned and adapted to the ion mobility range and elution time of the targeted analytes throughout the gas chromatographic run. This method was applied to a challenging mixture of 175 persistent organic pollutants (POPs) using a Bruker TIMS TOFpro II mass spectrometer equipped with a GC-APCI II source for sample separation and ionization, prior to TIMS-MS analysis.

The use of narrow ion mobility ranges in SWIM mode led to significantly improved resolving power (~40%) compared to the standard mode. This improved the separation of several critical GC coeluting isobaric and isomeric pairs. Overall, although all coeluting isobaric pairs could be separated in the ion mobility dimension, most coeluting isomeric pairs remained unresolved, despite the higher resolving power provided by the SWIM approach. Nevertheless, these results demonstrate the great potential of the integration of high-resolution ion mobility within GC-MS systems for the monitoring of organic pollutants.

P-19

Detection and determination of styrene oligomers (dimers and trimers) in foodstuff and food simulants using an automated LC-GC-MS/MS Method

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Abstract

Polystyrene have been playing an important role in packaging material for foodstuff for a long time. It is present in several products in direct contact with the food, as for example as sheets in sausage and cheese packaging, meal trays, thermal insulating layers, yogurt cups etc.

The broad application and the daily use on a massive scale of those synthetics based on styrene raises the question whether the production is compliant with Good Manufacturing Practices (GMP), also on a supra-regional level. Already in 2016, the critical limit for a single styrene oligomer was indicated with 50 µg/kg in food or food simulants (BfR statement 023/2016).

Styrene oligomers result from the manufacture of polystyrene and remain unintentionally compounds (non-intentionally added substances, NIAS) in the final product. Therefore, they may potentially merge to foodstuff upon contact.

The poster shows how styrene oligomers can be determined automatically.

P-20

Determination of glycerol triheptanoate (GTH) in animal feed: UHPLC-MSMS analysis preceded by microwave extraction

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Abstract

In the 1990s, the mad cow crisis highlighted the transmission of animal diseases due to the presence of inappropriate fats in the diet. In order to prevent animal by-products not intended for human consumption from returning to the food chain, European Regulation 1774/2002 identified glycerol triheptanoate (GTH) as a potential marker due to its chemical properties and ability to mix easily with fat-containing products. A GC-MS analytical method has been developed to detect the presence of GTH in food, but it has disadvantages such as its duration, cumbersome implementation and the use of large quantities of solvent during extraction.

In order to reduce the disadvantages of this method, an alternative approach has been developed within the CRA-W. The time-consuming and solvent-consuming Soxhlet extraction was replaced by microwave extraction, the purification of the extracted fat was discontinued, and the GC-MS was replaced by a UPLC-MSMS® analysis.

The first results indicate that microwave extraction makes it possible to recover all the fat present. This assessment was made on feed samples from interlaboratory testing (BIPEA). The chromatographic protocol implemented (Acquity UPLC® system coupled to a Quatro Premier XE quadrupole tandem mass spectometer) uses a 1.7 µm ACQUITY CSH Premier C18 column to easily separate the GTH from other glycerides.

The combination "Microwave Extraction / UPLC® MSMS" advantageously replaces the "Soxhlet – purification – GCMS" protocol for its speed of execution and the volumes of solvent consumed. It now remains to verify the potential of the method to reach the lowest detection thresholds, in order to easily highlight any attempt at fraud.

P-21

Analysis of triglycerides by UPLC/MSMS. Application in the case of bovine milk fat

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Abstract

Milk fat is a complex mixture of triglycerides. Some of these may have important functions in areas such as human health or the food industry. Identifying and/or quantifying these triglycerides is no easy task with liquid chromatography, due to the existence of numerous isomeric forms. The coelution of molecules of different triglycerides of equal mass, and also the coelution of molecules of different mass - a phenomenon due to the properties of certain triglycerides and observed in reverse-phase LC - make their detection virtually impossible with conventional detectors. Refractive index detection, or light scattering detection by evaporation of the mobile phase, do not allow isomer discrimination, even with sub-2µm separation columns.

Tandem mass spectrometry allows us to access another dimension of a chromatogram by providing the mass spectra of each group of triglycerides separated. Based on this new dimension, and above all on a selection of certified pure triglyceride standards, a more detailed characterization of fat extracts becomes possible.

The method developed involves milk fat extraction based on the protocol of Zhiqian L. et al. (2016). The chromatographic separation uses an Acquity UPLC® system coupled with a tandem mass spectrometer (Quatro Premier XE). The column is a UPLC® CSH Premier C18 2.1*100 mm, 1.7 µm and the mobile phase is based on a gradient composed of a mixture of water, acetonitrile and isopropanol with ammonium formate buffer and formic acid. Ten triglycerides representative of milk fat were selected and characterized by mass spectrometry. The analysis of different milk fat extracts shows the relevance of the choice of these standards but also illustrates the complexity of chromatograms: many compounds with a similar mass are found in the extract. An analysis with high-resolution mass spectrometry should provide new elements of answer by approaching the analysis under a lipidomics approach, dedicated to triglycerides.

P-22

Do ancient cereals and legumes differ in phytate content from modern counterparts? Greco-Roman KARANIS as a case study

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Abstract

Have you ever wondered what ancient world people used to eat in their daily lives? Was it more or less nutritious than modern foodstuffs? Cereals and legumes have been used as major foods for a long time. Our study in the context of the AGROS project, is focused on studying the nutritional and compositional analyses of ancient plant remains from Karanis to reconstruct the nutritional profiles of ancient crops, and to experimentally assess the composition and food safety of ancient foodstuffs, in comparison with modern counterparts. As we are studying raw plants, phytates are considered one of the important diverse groups of compounds to be analyzed. The colorimetric method was developed and validated for the determination of total phytates in barley, wheat, grasspea, lentil, lupine, and pea. Data analysis showed that significant differences were observed between phytate content in ancient and modern *lens culinaris*, and *Lupinus albus* (Egypt). In *Pisum sativum* var. *arvense* (Spain), and *Pisum sativum* (Karanis), the total phytate showed no significant difference. *Pisum sativum* (Spain and Jerusalem) showed a significant difference from *Pisum sativum* (Karanis). *Lathyrus sativus* (Spain, EU, and Karanis) showed no significant difference was observed in total phytate content. *Hordeum vulgare* ssp. *vulgare*, and *Hordeum vulgare* ssp. *distichon* (Jerusalem) showed no significant difference in total phytate with *Hordeum vulgare* ssp. *vulgare* (Karanis). The organic barley from the EU showed more phytate content compared to Karanis. *Triticum* sp. (bought from Morocco), Jerusalem, Greece, and *Triticum aestivum* ssp. *aestivum* (Egypt) showed no statistical significance difference with *Triticum turgidum* ssp. var. *durum* from Karanis. Both *Triticum* sp. and *Triticum turgidum* ssp. *dicoccon* (Spain) showed less phytate content than *Triticum turgidum* ssp. *durum* (Karanis). Furthermore, a UPLC-UV method is under development for the determination of individual inositol phosphates in cereals and legumes of ancient and modern origins.

P-23

Novel insight into the evolution of volatile compounds during dynamic freeze-drying of *Ziziphus jujuba* cv. Huizao based on GC-MS combined with multivariate data analysis

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Abstract

To understand the evolution of aroma in jujubes during dynamic freeze drying (FD), the relationship between aroma compounds, precursors, and related enzyme activities were analyzed. Fifty-three volatiles were identified during FD processing. After FD, the total aroma contents were increased from 11,004 to 14,603 μg/kg, ketones content was significantly decreased by 54.11%, resulted in the loss of creamy note in freeze-dried jujube (FDJ). Through the network analysis, serine, glycine, proline, valine, cysteine, arginine, glutamic acid, lysine and leucine had the significant correlation with pyrazines, dominated the roasty note of FDJ. Linoleic acid, α-linolenic acid and oleic acid with lipoxygenase had important effects on the increase of esters (from 412 to 9,486 μg/kg), contributed fruity and sweet notes of FDJ. Besides, through the Mantel test, the influence degree of factors on the formation of FDJ aroma was ranked as temperature > enzyme activity > fatty acids > amino acids.

P-24

A comparative analysis of neurotoxin β-ODAP and its non-toxic α-isomer in modern and ancient archaeological remains of grass pea by HPLC-MS/MS

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Abstract

Lathyrus sativus (grass pea) is a high-yielding, drought-resistant high protein legume consumed as a food in the Mediterranean, North Africa, Northern India, and neighbouring countries. Its development into an important food, has been hindered by the presence of the antinutritional β-N-oxalyl-L-α,β-diaminopropionic acid (β-ODAP) in the seeds which, if consumed in large quantities for prolonged periods, can cause irreversible paralysis. The aim of the current study is to determine the levels of α, β, and total ODAP in modern samples of grass pea seeds collected from different locations, which will be compared to archaeological specimens of grass pea from Greco-Roman Egypt to assess diachronic trends in the presence and ubiquity of this antinutrient. To fulfil these goals, a simple, fast, and accurate HPLC-MS/MS method was developed using a HILIC-N column at 25 °C, injection volume of 20 µL and isocratic elution of 90% (H2O/1.5%HCOOH) and 10% (acetonitrile/1.5%HCOOH) at flow rate of 0.50 mL/min, for 10 min. The analysed compounds (α-, and β-ODAP) and the internal standard (L-glutamic acid 15N) were detected using MRM mode and in positive ESI, and quantification was performed using two mass transitions (177>116 and 177>105) for α-, and β-ODAP. The proposed method is fully validated and offers good linearity, sensitivity, accuracy, repeatability, and precision. The application of the method to real samples is in progress. The current study will help to chart and monitor the level of the toxic β-ODAP in grass pea populations in different locales, so the consumption of grass pea can be optimized. This research is conducted within the context of the EoS project AGROS that assesses the nutritional composition of ancient crop remains and compares these with modern crops. The current study will provide the first empirical data on the level of antinutritional factor β-ODAP in ancient archaeological raw ingredients.

P-25

Automated Sample Preparation and Measurement for Dioxin analysis

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Abstract

Dioxins are a class of very toxic compounds found throughout the world in the environment. Equipment sensitivity is of great importance for the analysis of low concentrations of these highly toxic compounds. Historically, analysis and detection of dioxins was done with magnetic sector-type high-resolution mass spectrometers (HRMS). However, in recent years, the performance of triple quadrupole mass spectrometers (MS/MS) has improved significantly.

The development of the Boosted Efficiency Ion Source (BEIS) offers compound specific sensitivity up to 4 times greater than previous ion sources and provides accurate quantitation of dioxins at levels comparable to HRMS. Detection limits as low as 20 fg for Tetrachlorodibenzo-p-dioxin (TCDD) were achieved. In this study, we analyzed dioxins in about 250 samples of approximately 40 types of food and animal feed products using a GC-MS/MS with BEIS. We also evaluated the number of analyses possible while maintaining sensitivity at low concentrations in order to verify the durability of the GC-MS/MS instrument.

P-26

Diverse approaches to capturing bacterial volatiles in Aphid Honeydew: Methodological comparisons

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Abstract

Aphid honeydew is a valuable carbohydrate source and host location cues to beneficial insects. Composed primarily of sugars and amino acids, it creates an optimal environment for microbial growth. Microbial volatile organic compounds (mVOCs) in honeydew play various roles in interactions between herbivores, microbes, and natural enemies. These compounds aid in locating food sources, recognizing host/prey, and stimulating oviposition, indirectly contributing to pest control. However, the identification and characterization of honeydew volatiles and associated mVOCs lack standardization and sufficient research. This preliminary research utilized SPME analysis to investigate honeydew volatiles using CWR-PDMS and CAR-PDMS fiber types. Dynamic headspace collection and SPME analysis were employed to capture mVOCs from bacteria associated with honeydew. This research provides new insights into the importance of selecting suitable extraction methods for volatile compounds in aphid honeydew. For the first time, it underscores the criticality of considering various factors such as the method employed, the fiber, and the sorbent material used. By thoroughly assessing multiple methods, this research reveals the strengths and weaknesses inherent to each approach. The observed differences unequivocally demonstrate that these methodological considerations profoundly impact the accuracy and reliability of the extraction process. SPME emerges as the most appropriate method due to the high concentration of mVOCs found in aphid honeydew and the ability to analyze small sample quantities. However, further investigations are required to optimize the protocol and establish standardization across all honeydew types.

P-27

Innovative Solutions to Critical Liquid Chromatography Workflows Employing Porous Graphitic Carbon UHPLC Columns

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Abstract

Porous Graphitic Carbons (PGCs), employed as a stationary phase for HPLC, have been available commercially for nearly 30 years. At the time, columns made with these new, innovative materials offered some significant advantages to silica-based columns such as wide pH operating ranges, increased temperature stability, and no possibility of secondary interactions of analytes that many silica columns suffer from due to residual silanol species on the base silica particle. Despite some of these advantages it has not garnered the same popularity as conventional silica-based stationary phases, as the intricacies of working with carbonaceous supports is not as straightforward. This seminar will discuss strategies for using PGC columns to analyze polar compounds and best practices to employ to maximize the performance of the columns. After a short introduction to PGC materials, the ability of the column to analyze complex samples will be demonstrated with applications including nitrosamine analysis in active pharmaceutical ingredients, glycan characterization of biotherapeutics, and the analysis of sugar-modified nucleosides, amongst others. In addition, aspects of method optimization and validation using PGC columns will be showcased with the above applications, illustrating the stationary phase's ability to resolve current challenges in liquid chromatography.

P-28

Novel Approaches for Critical Quality Attribute Determination for Therapeutic Antibodies, Antibody-Drug Conjugates, and Oligonucleotides

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Abstract

The analysis of pharmaceutical drugs for impurities is a crucial task performed by pharmaceutical companies. Any impurity present in a drug formulation can cause a range of side effects in patients, from reduced efficacy in treating the disease all the way to allergic response and death of the patient. This task has become even more prominent with the emergence of biotherapeutics where these drugs are produced in living cells and could be exposed to multiple reactions which could change the structure or activity of the molecule. Due to this complexity, combined with the much larger, overall size of the molecules when compared to "small molecule" pharmaceuticals, the need for novel methods to fully characterize these molecules is desired. This paper focuses on novel approaches in characterizing three, emerging classes of biotherapeutics: monoclonal antibodies (mAbs), antibody-drug conjugates (ADCs), and oligonucleotides. Details on approaches to improve throughput and efficiency in determining aggregation amount and charge variants will be outlined. In addition, a novel, mass spectrometry (MS) compatible size exclusion method for determining the drug-antibody ratio (DAR) of an ADC will be explained which will enable the researcher to not have to only rely on high salt, hydrophobic interaction chromatography (HIC) methods. Finally, aspects of oligonucleotide characterization will be highlighted, including strategies for proper mobile phase selection and alternatives to the use of ion pair reversed phase methods.

P-29

Characterization and differentiation of Chinese 'Baijiu' liquor applying SPME coupled to comprehensive two-dimensional chromatography and Time-of-Flight Mass Spectrometry (GC×GC-TOFMS)

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Abstract

Baijiu is a traditional Chinese spirit with a complex pattern of volatile organic compounds (VOCs). The rich aroma results from the relatively complex and multilayered manufacturing process, including fermentation and various technological processing steps. In general, Baijiu can be classified according to the aroma type (e.g., strong, light, rice, sauce) which is associated with a distinct taste.

Comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC-TOFMS) was used to differentiate Baijiu samples in terms of their aroma type and origin (region). In total, 10 Baijiu samples were investigated: VOCs were extracted by head-space solid phase micro-extraction (HS-SPME) followed by GC×GC-TOFMS analysis. The characteristic Baijiu profiles displayed a wide range of concentration levels, which challenge the accurate detection and identification of compounds of very low abundance using a classical one-dimensional GC-MS approach. In this study, we evaluate the use of comprehensive two-dimensional GC×GC-TOFMS to significantly improve the separation, detection, and therefore identification of species in Baijiu to provide a higher quality and more informative characterization ability.

The optimized analytical parameters allowed for a comprehensive characterization of the individual Baijiu samples. Beyond that, a non-targeted differentiative analysis was performed to determine trends and patterns among the different Baijiu types. The comparison of the aroma profiles and the data analysis was facilitated by the means of a supervised statistical analysis tool, called ChromaTOF® Tile. Group type separation according to their respective class in terms of aroma-type and origin was obtained and statistically significant differences were easily highlighted.

P-30

Unlocking the aroma compounds of pistachios using the power of multi-dimensional gas chromatography

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Abstract

The quality and consumer acceptance of pistachios heavily rely on their distinctive aroma, which serves as a crucial organoleptic characteristic. Similar to other natural products, the aroma of pistachios is influenced by numerous factors, including the cultivar, geographical origin, harvesting conditions, and storage methods. The majority of pistachio production occurs in countries with warm and arid climates. Notably, Iran, the United States (USA), Italy, Greece, Tunisia, Turkey, Syria, and Spain stand out as the world's leading pistachio producers. Characterizing the unique aroma profiles of pistachios is essential not only for consumer acceptance but also for establishing standardized production processes in the industry. In this particular study, the volatile organic compounds (VOCs) present in pistachios sourced from various geographic locations were evaluated. The assessment employed a high-capacity concentration (HCC) tool called HiSorb™, which bridges the gap between solid phase micro-extraction (SPME) and stir bar sorptive extraction (SBSE), thereby enhancing sensitivity and repeatability through its automated and user-friendly interface. Different HiSorb™ probes were assessed to determine the optimal parameters, including extraction temperature and duration. Subsequently, the VOCs extracted using HiSorb™ were subjected to two-dimensional comprehensive gas chromatography-mass spectrometry (GC×GC-MS) analysis, utilizing a reversed fill/flush flow modulator. The use of multidimensional gas chromatography enhances the separation power and maximizes the amount of information obtained, resulting in a comprehensive chromatographic fingerprint of the VOCs present in pistachios.

P-31

Exploration of the saponification conditions for mineral oil analysis through the utilization of microwave-assisted saponification/extraction

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Abstract

Mineral oil hydrocarbons are a class of pollutants that potentially possess harmful properties, particularly the aromatic hydrocarbons (MOAH) subset. The process of analytical determination is found to be associated with a considerable degree of variability, mainly attributable to the procedures involved in the sample preparation phase that requires enrichment and purification, alongside the interpretation of chromatograms. In recent years, efforts have been undertaken to automate the chromatogram interpretation, resulting in a variability decrease.

Regarding the sample preparation, two interlaboratory trials conducted in the previous year – one by the JRC for infant formula, and another by the DGF for oil and fat – have highlighted the challenge of achieving low sensitivity in detecting the MOAH fraction in fat samples, resulting in a limit of quantification (LOQ) of 2 mg/ml. An issue noted was the observed discrepancy in the recovery of the internal standards. It can be observed that TBB exhibits a superior recovery compared to the MN standards. Indeed, the mean ratio of TBB compared to the MN standards stands at 1.15. One issue encountered was that, in one trial, TBB yielded superior recovery outcomes while 2MN resulted in better recoveries in another, indicating that the recovery of contamination could vary according to its specific composition. The objective of minimizing variability was addressed through the use of an innovative saponification technique, which leveraged the benefits associated with microwave-assisted saponification/extraction. Subsequently, evaluations were conducted on the partitioning behaviour of internal standards, across a diverse range of matrices and saponification conditions. In summary, the observed ratio disparity among all matrices scrutinized was diminished from a range of 1.11 to 1.18 to a range of 1.02 to 1.08.

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P-32

Qualitative screening of catalytic pyrolysis wood oil by means of GC×GC-TOFMS, soft ionization, and different columns setup

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Abstract

During biomass pyrolysis, catalytic processes are needed to increase the H C ratio of the products since oxygen-containing compounds limit the use of the oil as fuel due to its corrosion properties and instability Here GC × GC TOFMS and supported by soft ionization has been exploited for the characterization of volatile and semi-volatile compounds in catalytic pyrolysis wood oil Two column sets up have been explored, and a reverse-phase combination has also been optimized for the separation of the oxygenated compounds from the hydrocarbon matrix. This approach allowed explaining the bio-oil composition and checking the efficiency of catalytic pyrolysis applied to reduce the concentration of the oxygenated compound.

P-33

Contribution of atmospheric pressure chemical ionization mass spectrometry for the characterization of bio-oils from lignocellulosic biomass: comparison with electrospray ionization and atmospheric pressure photoionization

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Abstract

Bio-oils obtained from lignocellulosic biomass pyrolysis present a very promising alternative to replace petroleum-based fuels. At the molecular level, these materials are highly complex organic mixtures comprising thousands of species covering a large range of mass and polarity. Compared to petroleum, they present a high amount of oxygen containing compounds, limiting their direct use in the classical refining system. To understand and improve both the conversion and upgrading processes, an advanced molecular description of the raw and upgraded bio-oils is required. The most powerful technique for the molecular characterization of such sample is Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS), thanks to its very high mass accuracy and resolving power. It allows assigning unambiguously a unique molecular formula to each m/z signal.

P-34

Enhanced sample preparation of environmental matrices with microwave assisted extraction

Diego Carnaroglio

Milestone, Sorisole, Italy

Abstract

Microwave technology is a well-established and widely used ally in sample preparation processes. Among several approaches available to overcome the bottleneck of analytical procedures, **Microwave Assisted Solvent Extraction** (MASE) entails unique advantages. It allows to work at elevated temperature and pressure conditions in a safe environment, **speeding up the extraction processes**. The higher efficiency gained with MASE enables to **reduce the solvent usage** developing more sustainable procedure and miniaturizing the process.

MASE finds its perfect application in the sample preparation of water insoluble or slightly water-soluble organic compounds in environmental samples such as soils, clays, sediments, sludges, and solid waste. **Semivolatile organics, organochlorine pesticides, PAHs, PCBs, phenoxyacid herbicides, phenols and dioxins** can be efficiently extracted with MASE. These extraction procedures are described here below, with a special focus on the analysis of dioxins, which is one of the most challenging, or even not achievable, application.

P-35

Fast and reliable fatty acid methyl ester (FAME) determination in foodstuff by microwave sample preparation

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Abstract

The determination of fat content in food samples is a common task for food industry quality control labs and for third party contract labs. **Fatty Acid Methyl Ester** (FAME) analysis is commonly used to calculate saturated, monounsaturated, and polyunsaturated fat contents. Several official methods are available, based on obsolete and time-consuming techniques, which are often matrix-specific.

Microwave assisted FAME protocols, with ETHOS X **microwave extraction system**, are applicable to several food matrices and allow the **determination of total fat or free fat** depending on the method applied. Thanks to ETHOS X, labs can **reduce the analysis costs** and **improve the turnaround time** with higher productivity, less time and solvent consumption.

P-36

Comparison of different extraction methods for the determination of fatty acid methyl esters in mussels' samples

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Abstract

The profiling of fatty acids (FAs) involves an analytical approach that offers detailed information regarding the qualitative and quantitative distribution of FAs in food products. This technique, when combined with high-capacity analytical methods, aids in addressing numerous questions related to the nutritional quality and authenticity of food. In natural samples, FAs are primarily found in esterified forms as triglycerides, necessitating their conversion into fatty acid methyl esters (FAMEs) prior to gas chromatography analysis for precise profiling. Prior to any derivatization reaction, lipid extraction from complex matrices, apart from pure fats and oils, is necessary. In this work, three methods for the extraction and derivatization of FAMEs are used. In particular, the fatty acids profile obtained with the microwaves-assisted extraction and derivatization (MAED) was compared with the one obtained from the conventional FAMEs preparation method. The microwave-assisted method proved to be fast, simple, and effective for analysing complex samples like mussels. The FAMEs were subsequently analysed using reversed fill/flush differential-flow modulation comprehensive two-dimensional gas chromatography (GCxGC) coupled with flame ionization detection (FID) to identify and quantify individual fatty acids. GCxGC analysis offers superior separation power compared to one-dimensional GC and generates structured chromatograms based on the chemical patterns, enhancing the reliability and accuracy of identification. Additionally, the environmental impact of the method was evaluated based on the recently published PrepAGREE criteria, demonstrating superior performances compared to official methods in terms of greenness.

P-37

Potentialities of High-Capacity-Headspace-Extraction followed by GC×GC-qMS to better appreciate coffee brew note

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Abstract

The distinctive scent profile of food is influenced by volatile and semi-volatile organic compounds, which also provide a distinctive fingerprint that may be used to assess the quality and authenticity of foods.

Solid-phase microextraction (SPME), which combines the ease of use with a high enrichment factor, is by far the most used sample technique. To increase sample throughput, this approach frequently necessitates a trade-off between sensitivity and extraction time.

New analytical tools have emerged by the time to improve the sensitivity with the arrival of commercial stir-bare sorbent extractor (SBSE) and SPME-arrow system. The letter one having the advantage of being fully automatable as SPME but less sensitive than the SBSE. In 2016, a new probe-like tool (HiSorb), combining the sensitivity of SBSE and the automation of SPME, has appeared. For a long time, this tool was limited to the PDMS-only sorbent phase (which already boasts higher sensitivity than SPME-triphasic), until the recent appearance of new phases.

This poster discusses the use of a higher sorbent volume to improve sensitivity as well as the advantage of using different sorbent phase. A comparison between SPME and HiSorb and their respective sorbent phases will be carried out based on their ability to capture coffee brew volatile using GC×GC-qMS.

P-38

Analysis of Semi-Volatiles Organic Compounds in water samples with a fully automated multi fiber extraction approach, preliminary results.

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Abstract

Water analysis for semi-volatile organic compounds (SVOCs) is a challenging and labour-intensive task, due to the low limits of quantitation required. In order to reduce the amount of space and time required, to further minimize human errors and environmental impact of analysis process, a fully automated and modular at instrument sample preparation and extraction method by solid phase microextraction (SPME) before GC-MS/MS analysis is proposed for polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), phenols, polybrominated diphenyl ethers (PBDE), aromatic amines and pesticides. Working with both traditional and arrow SPME fibers automatically switched when needed thanks to Multi Fiber Exchange (MFX) all the extraction parameters have been optimized in order to minimize analysis time and maximize sensitivity for all proposed analytes. To increase versatility 2 different approaches have been evaluated: headspace-SPME sampling (HS-SPME) ad/or direct immersion-SPME (DI-SPME), both are proposed for some analytes.

Preliminary studies have shown excellent results and possibility for further improvement in the nearest future.